Interfacial Thermodynamics of Polyolefin Blends and Copolymers

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Received May 16, 1994; Revised Manuscript Received September 9, 1994[⊗]

ABSTRACT: Some universal aspects of interfacial thermodynamics in nearly athermal blends and block copolymers are discussed. While the primary application of the theoretical analysis is to interfaces between polyolefins, the analysis also applies to interfaces between chemically identical but architecturally asymmetric components, such as linear and comb polystyrenes. Specific cases treated are interfaces between linear and short-branched polyolefins and interfaces between linear and comb polymers. For both situations, we derive expressions for the interfacial tension and profile and provide numerical results where appropriate. The implications for the phase diagrams of polyolefin block copolymers are also briefly discussed.

I. Introduction

There has recently been considerable interest in whether the bulk miscibility of nearly athermal polymer blends, such as mixtures of polyolefins, can be correlated solely on the basis of structural differences between pure components in the melt.[1-4] The structural differences that have been argued to be relevant to miscibility can be broadly categorized as arising from either "conformational" or "architectural" asymmetry,[5] the former referring to differences in the melt conformational and packing states of the pure components being mixed and the latter reflecting gross differences (over mesoscopic distances) in architectures of the components, e.g., linear versus branched.

In the case of model polyolefin blends that contain only linear components, or components with at most short (e.g., propyl or ethyl) side branches, the conformational asymmetry notion has been reasonably successful in correlating the liquid state miscibility of a number of homopolymer and random copolymer blends,[1,2,6] as well as the order–disorder transition of a series of model diblock copolymers.[1,7] While there appear to be exceptions,[2] a growing body of evidence suggests that there exists a large number of systems that can be prepared by the hydrogenation of butadienes, isoprenes, and even styrene, which conform to the principle that miscibility improves as components are made more similar in their conformational and packing properties.[8]

There have been several theoretical attempts to quantify this principle, most recently by Schweizer[4] and by Fredrickson, Liu, and Bates.[3,5] Our approach, which is more coarse-grained and less ambitious than that of Schweizer, has been to assume incompressibility at scales larger than a cutoff monomer size, Λ^{-1}, and compute the first fluctuation corrections (one-loop order in field theory) to Flory–Huggins mean-field theory. While we refer the interested reader to ref 5 for details of the theory, we comment here that our approximate treatment of the many-body problem is a type of "random phase approximation" (RPA) in the sense of classical liquid state theory.[9] In this regard, we go a step beyond "polymer RPA",[10] which is a mean-field theory consistent with Flory–Huggins theory. Thus, while $\chi = 0$ for an athermal blend in either Flory–Huggins theory or polymer RPA, our theory leads to a positive effective χ (of entropic origins) associated with mixing components different in conformations or architecture.

For a binary blend of molten linear components 1 and 2, we obtained the following expression for the interaction density (proportional to the effective χ parameter) arising from conformational asymmetry:[3,5]

$$\alpha_\epsilon = \frac{\Lambda^3}{24\pi^2}\left[\frac{1-(\beta_1/\beta_2)^2}{\phi + (1-\phi)(\beta_1/\beta_2)^2}\right]^2 \qquad (1.1)$$

In this expression, ϕ is the volume fraction of component 1 and β_i for $i = 1$ or 2 are pure-component parameters that were first introduced by Helfand and Sapse[11] in a different context:

$$\beta_i^{\,2} \equiv \frac{b_i^{\,2}}{6\nu_i} = \frac{R_i^{\,2}}{V_i} \qquad (1.2)$$

The quantities appearing in this expression are the statistical segment length, b_i, statistical segment volume, ν_i, mean-squared radius of gyration, R_i^2, and total molecular volume, V_i, of a chain of component i in its pure melt at the temperature and pressure of interest. The final expression in eq 1.2, a ratio of two measurable quantities, makes it clear that β_i is independent of how statistical segments are defined. From this definition, it is also clear that β_i is largest for a linear component, such as polyethylene (PE), whose coil dimensions increase rapidly with increasing molecular weight or volume, and smaller for a short-branched component, such as poly(ethylethylene) (PEE), for which much of the molecular volume is carried by branches. Temperature-dependent values of β_i have been tabulated for a large number of model polyolefins by Gehlsen and Bates[7] and also by Fetters et al.[12] In this regard, we note that the "packing length" p introduced by the latter authors and correlated with melt viscoelastic properties is proportional to β^{-2} for a given pure component.

In spite of the fact that eq 1.1 depends on a monomer-scale cutoff Λ whose value the theory does not address, the remaining factor in eq 1.1 is *universal* for all polymer blends with comparable values of the composition ϕ and "conformational asymmetry" parameter $\epsilon \equiv$

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1994.

0024-9297/94/2227-7382$04.50/0

$(\beta_1/\beta_2)^2$. It is clear from eq 1.1 that blends in which ϵ differs significantly from unity will have a large interaction density α_ϵ (i.e., Flory χ parameter) and hence will be immiscible. In particular, since α_ϵ is to be compared with the ideal entropy of mixing per unit volume at the point of phase separation, ϵ may differ from unity by no more than $O(N^{-1/2})$ for miscibility to be achieved (N is a characteristic degree of polymerization). This prediction is in accordance with a growing body of experimental literature on polyolefins.[1,2,7] We also note that the form of eq 1.1 is quite robust in the context of a loop expansion in polymer field theory[13] and resembles expressions derived by Schweizer[4] on the basis of polymer RISM theory. The latter theory has the advantage of naturally imposing a cutoff through the inclusion of realistic hard-core potentials, yet is considerably more difficult to implement.

The theory described above has been generalized[5] to analyze the bulk miscibility of certain "architecturally asymmetric" polymer blends. In particular, mixtures of chemically identical linear and star polymers have been treated, as well as mixtures of chemically identical linear and comb polymers. For such systems, e.g., a mixture of linear and star polystyrene, the local conformational properties of the branches and linear backbones are precisely matched, but larger-scale intramolecular correlations differ between components. When such components are forced to mix at constant density, the native conformational states are disrupted and a positive excess (entropic) free energy of mixing is obtained. This excess contribution, and hence the tendency for phase separation, naturally increases with both the density and functionality of branch points on the second component. As demonstrated by explicit calculations,[5] the excess contribution to the free energy can be represented by expressions similar to eq 1.1, but which are *completely universal and contain no cutoff*, i.e., Λ. This absence of a cutoff is due to the fact that the dominant liquid state correlations that contribute to α_ϵ for such architecturally asymmetric blends are associated with length scales much larger than the monomer size. Thus, for such systems we anticipate that our field-theoretic and the RISM-based approaches should yield coincident results and, more importantly, that *quantitative* theoretical predictions can be made for blend miscibility.

In the present paper, we extend the above methodology for analyzing the bulk phase behavior of nearly athermal polymer blends to study the interfacial thermodynamics of such systems. In particular, we consider binary blends of polyolefins (or other applicable components) that possess sufficient conformational or architectural asymmetry for phase separation to occur. On the basis of a suitably constructed Cahn–Hilliard type theory, we analyze the equilibrium interfacial tension and composition profile of a planar interface between the two coexisting phases. We pay particular attention to the universal (system-independent) predictions that arise, especially the dependence of the tension and profile shape on the conformational asymmetry parameter $\epsilon = (\beta_1/\beta_2)^2$ and on any architectural asymmetries. In the next section, we restrict our consideration to interfaces formed by mixtures of linear or nearly linear short-branched polyolefins, such as interfaces between PE and PEE. In section III, we extend this analysis to interfaces formed by mixtures of chemically identical linear and comb polymers, e.g., a linear polyisoprene–comb polyisoprene interface. Finally, in section IV we discuss how these results for the interfacial thermodynamics of polyolefins and related systems are important for understanding the phase diagrams and morphologies of polyolefin block copolymers.

II. Interface between Linear Polyolefins

In the present section we consider a phase-separated blend of two linear or short-branched polyolefins, such as polyethylene (PE) mixed with poly(ethylethylene) (PEE). For simplicity, we imagine a single planar interface separating the two bulk coexisting phases with surface normal taken to lie along the z-axis. We shall be primarily concerned with the case of strong segregation,[11,14] for which the bulk phases are nearly pure in the two components and the interfacial thermodynamic properties are approximately molecular weight independent.

For a *homogeneous* mixture of two such polyolefin components, it was argued previously by Fredrickson, Liu, and Bates[5] that the free energy density of mixing can be written in the form

$$\Delta F = \Delta F_0 + \Delta F_E \tag{2.1}$$

where the *ideal* entropy of mixing is given by the usual Flory–Huggins expression

$$\frac{\Delta F_0}{k_B T} = \frac{\phi}{V_1}\ln\phi + \frac{1-\phi}{V_2}\ln(1-\phi) \tag{2.2}$$

and the *excess* contribution arising from conformational asymmetry is given by[15]

$$\frac{\Delta F_E}{k_B T} = \frac{1}{4\pi^2}\int_0^\Lambda dk\, k^2 \ln\left[\frac{\phi S_1(k) + (1-\phi)S_2(k)}{S_1(k)^\phi S_2(k)^{1-\phi}}\right] \tag{2.3}$$

The parameter Λ in this expression is the cutoff wavenumber discussed above and $S_i(k)$ is the structure factor of a single chain of *pure component i*, normalized as discussed in ref 5. The dominant contribution to the integral in eq 2.3 arises from wavevectors k that greatly exceed the inverse of the radius of gyration scale;[3,5] in this regime, assuming Gaussian statistics, the $S_i(k)$ reduce to

$$S_i(k) \approx \frac{2}{\beta_i^2 k^2} \tag{2.4}$$

Substitution of this expression into eq 2.3 leads to the following result for the excess free energy density:

$$\frac{\Delta F_E}{k_B T} = \Lambda^3 f_E(\phi,\epsilon) \tag{2.5}$$

where

$$f_E(\phi,\epsilon) = \frac{1}{24\pi^2}\ln\left[\frac{\phi + \epsilon(1-\phi)}{\epsilon^{1-\phi}}\right] \tag{2.6}$$

and $\epsilon \equiv (\beta_1/\beta_2)^2$ with β_i defined in eq 1.2.

Equation 2.5 plays a similar role as the usual excess term $\chi\phi(1-\phi)$ in Flory–Huggins theory; in the present case the "bare" Flory χ parameter is zero because of our athermal assumption, but eq 2.5 generates an effective χ (or interaction density α_ϵ) of entropic origin. The unusual form of eq 2.6 arises from conformational asymmetry effects that are assumed to be dominant in the present case of nearly athermal blends. $f_E(\phi,\epsilon)$ vanishes linearly with ϕ or $1 - \phi$, respectively, in the limits $\phi \to 0$ and $\phi \to 1$. For weak conformational asymmetry, i.e. $\epsilon = 1 + \delta$ with $\delta \ll 1$, this entropic excess free energy takes the conventional Flory–Huggins (regular solution) form: $f_E \approx (1/48\pi^2)\delta^2\phi(1 - \phi)$. An effective interaction density, α_ϵ, which is the quantity measured in scattering experiments and relevant to the spinodal, can be defined as

$$\alpha_\epsilon \equiv -\frac{1}{2k_BT}\frac{\partial^2 \Delta F_E}{\partial \phi^2} \tag{2.7}$$

By explicitly performing the indicated composition derivatives on eq 2.6, our earlier result for α_ϵ given in eq 1.1 is recovered. We also note that the spinodal equation, defining the bulk thermodynamic stability limit of a single homogeneous phase, is given by

$$\frac{1}{\phi V_1} + \frac{1}{(1-\phi)V_2} - 2\alpha_\epsilon = 0 \tag{2.8}$$

Thus, as discussed in the Introduction, phase separation will proceed when α_ϵ is characteristically larger than the largest reciprocal molecular volume, $1/V_i$. In the specific case of PE mixed with PEE, this condition is always met; for example $\epsilon = (\beta_{PE}/\beta_{PEE})^2 \approx 2.53$ at 150 °C,[7] which implies that $\alpha_\epsilon \sim \Lambda^3 \sim 1/v_i \gg 1/V_i$. It follows that such blends will be strongly segregated, with nearly molecular weight independent interfacial properties.

With this background on the bulk thermodynamic properties of a homogeneous mixture of two polyolefin components, we now turn to the analysis of a flat interface in the strongly segregated regime. The method employed is a variant of classical Cahn–Hilliard theory,[16] generalized to treat polymer interfaces in the strong segregation regime by Roe[17] and Broseta et al.[18] In principle, the more powerful self-consistent field method of Helfand and Sapse[11] could be used, but the present approach gives the same asymptotic results in the strong segregation limit.[18]

We proceed by following the approach of Cahn and Hilliard[16] and express the interfacial tension γ as the extremum (minimum) of the following functional with respect to variations in the composition profile $\phi(z)$:

$$\mathcal{F}[\phi] = \int_{-\infty}^{\infty} dz \left\{ \Lambda^3 f_E(\phi,\epsilon) + \left[\frac{\beta_A^{\;2}}{4\phi} + \frac{\beta_B^{\;2}}{4(1-\phi)}\right](d\phi/dz)^2 \right\} \tag{2.9}$$

The first term in this expression, which is purely local in $\phi(z)$, describes the excess free energy associated with the fact that the interfacial region has compositions intermediate between those of the coexisting bulk phases. Because we restrict consideration to the strong segregation limit, the bulk phases have composition $\phi_+ = 1$ ($z \to \infty$) and $\phi_- = 0$ ($z \to -\infty$) and the ideal entropy of mixing terms in eq 2.1, which are $O(1/V_i)$ smaller than ΔF_E, can be neglected. The square-gradient terms in eq 2.9 reflect the conformational entropy penalty associated with the portions of the two types of chains that participate in forming the interface. The numerical coefficients have been chosen to provide an accurate description of narrow interfaces, as discussed by Broseta et al.[18] and Roe[17] (see also the discussion after eq 3.11).

It proves convenient to rescale the spatial variable in eq 2.9 by the following fundamental length scale (bare interfacial width):

$$\xi_0 = (\beta_A\beta_B)^{1/2}\Lambda^{-3/2} \tag{2.10}$$

Denoting the scaled variable by $x = z/\xi_0$, eq 2.9 can be rewritten in the form

$$\mathcal{F}[\phi] = \Lambda^{3/2}(\beta_A\beta_B)^{1/2}\int_{-\infty}^{\infty} dx\, [f_E(\phi,\epsilon) + \kappa(\phi,\epsilon)(d\phi/dx)^2] \tag{2.11}$$

where $\kappa(\phi,\epsilon)$ is the following dimensionless function:

$$\kappa(\phi,\epsilon) = \frac{1}{4}\left(\frac{\epsilon^{1/2}}{\phi} + \frac{1}{(1-\phi)\epsilon^{1/2}}\right) \tag{2.12}$$

Finding the extremum of the above functional is a standard problem in the calculus of variations. The minimizing composition profile is given implicitly by the equation

$$\int_{1/2}^{\phi(x)} d\phi\, [\kappa(\phi,\epsilon)/f_E(\phi,\epsilon)]^{1/2} = x \tag{2.13}$$

Moreover, the interfacial tension can be written as a simple quadrature:

$$\gamma/k_BT = 2\Lambda^{3/2}(\beta_A\beta_B)^{1/2}\int_0^1 d\phi\, [f_E(\phi,\epsilon)\kappa(\phi,\epsilon)]^{1/2} \tag{2.14}$$

The universal features of the equilibrium interfacial profile are now clearly apparent. The composition profile, when expressed as a function of the scaled coordinate $x = z/\xi_0$, is a universal function of x for all polymer blends with the same value of the conformational asymmetry parameter $\epsilon = (\beta_A/\beta_B)^2$. In Figure 1, we illustrate three such profiles for different values of ϵ. As $\epsilon \to 1$, the interfacial width ξ diverges like $\xi \sim \xi_0/|1 - \epsilon|$, while it is bounded for any $\epsilon \neq 1$. Actually, when $|1 - \epsilon| \sim N^{-1/2}$ (N is a characteristic degree of polymerization), the interface becomes too broad for the present theory to be quantitative. Moreover, the homogeneous phase regains stability in this regime of ϵ very near unity. For more typical values of ϵ, the interfacial width is of order ξ_0 and we note that the interface shape is asymmetric about $x = 0$ (defined as the midpoint of the profile, $\phi(0) = 1/2$). In particular, the large β component penetrates more deeply into the small β phase than the reverse. This feature is a consequence of the compositional asymmetry of $f_E(\phi,\epsilon)$: a large-β (linear) chain is more miscible with a small-β (short-branched) melt than a comparably small-β chain is with a large-β melt. Finally, we note that a similar trend was predicted by Helfand and Sapse,[11] but the asymmetry calculated by these authors was less pronounced due to their use of the conventional Flory–Huggins excess free energy density, $f_E = \chi\phi(1 - \phi)$.

The universal properties of the interfacial tension are readily deduced by rewriting eq 2.14 in the form

$$\gamma = k_BT\Lambda^{3/2}(\beta_A\beta_B)^{1/2}H(\epsilon) \tag{2.15}$$

where

$$H(\epsilon) = 2\int_0^1 d\phi\, [f_E(\phi,\epsilon)\kappa(\phi,\epsilon)]^{1/2} \tag{2.16}$$

Thus, aside from the nonuniversal prefactor, $\Lambda^{3/2}$, the variation of the interfacial tension with the asymmetry parameter ϵ is described by the universal dimensionless function $H(\epsilon)$. In Figure 2 we provide a plot of this function obtained by performing the integral in eq 2.16 numerically. As expected, the tension vanishes at the

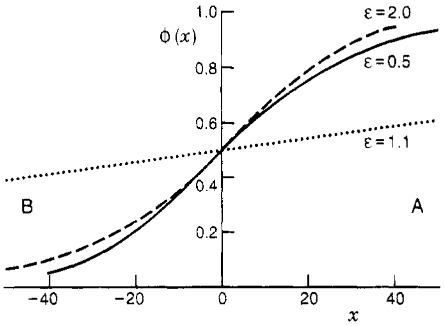

Figure 1. Composition profile $\phi(x)$ of conformationally asymmetric blends obtained by numerical integration of eq 2.13. The dashed, solid, and dotted curves correspond, respectively, to values of $\epsilon \equiv (\beta_1/\beta_2)^2$ equal to 2.0, 0.5, and 1.1. The dimensionless spatial coordinate $x = z/\xi_0$ is scaled by the bare interfacial width ξ_0, defined in eq 2.10.

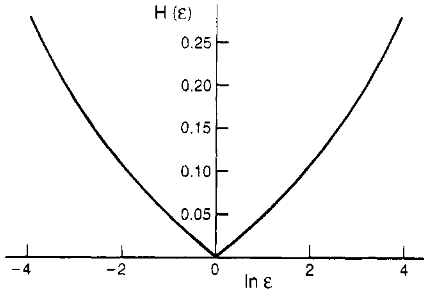

Figure 2. Dimensionless function $H(\epsilon)$ obtained by numerical integration of eq 2.16. The interfacial tension, which is proportional to $H(\epsilon)$, vanishes at the point of conformational symmetry, $\epsilon = 1$.

point of conformational symmetry, $\epsilon = 1$, and grows symmetrically and monotonically as ϵ departs from unity. In principle, this quasi-universal behavior could be tested by experimental studies of interfacial tension in a series of polyolefin random copolymers, such as PE−PEE copolymers. By measuring the random copolymer tension against a second homopolyolefin, e.g., polypropylene, as a function of copolymer composition (hence varying the effective β of the random copolymer[5]), it should be possible to examine the validity of eq 2.15.

As a final comment, we note that both the interfacial tension and the composition profile are predicted to vary with temperature not only because of explicit factors of k_BT but also because the β_i and hence ϵ vary with temperature. Explicit expressions for the temperature dependence of these pure-component parameters for a number of polyolefins have been given in the literature.[1,12] The cutoff, Λ, will in general also vary with temperature, although perhaps in a predictable manner.[24]

III. Interface between Linear and Comb Polymers

In the present section we generalize the above results for "conformationally asymmetric" interfaces to interfaces between "architecturally asymmetric" components. In particular, we treat the specific case of a molten mixture of linear and comb polymers that are otherwise *chemically identical*. Component 1 is taken to be a linear polymer. Component 2 is a comb polymer with the architecture shown in Figure 3; we adopt a simple model of a comb in which branches (teeth) of degree of polymerization L are equally spaced every L monomers along the main backbone. The degree of polymerization of the linear chain is denoted by N_1 and the degree of polymerization of the *backbone* of comb component 2 is denoted by N_2. We shall assume throughout that $N_1, N_2 \gg L$ but that L is large enough for the conformational properties of the teeth to be described by Gaussian statistics. Since the two components are assumed chemically identical on the monomer scale, a single statistical segment length, b, and a single segment volume, ν, suffice to specify the local conformational and packing properties of the blend.

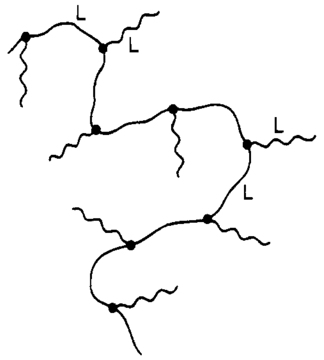

Figure 3. Schematic architecture of the comb polymer considered in section III. Each polymer has a branch of L statistical segments, equally spaced every L statistical segments along the backbone. The total backbone degree of polymerization is denoted N_2. The branches (teeth of the comb) and backbone are assumed to be chemically identical, with statistical segment length b and segment volume ν.

For such a linear−comb mixture, it was argued in an earlier paper[5] that the interaction density defined in eq 2.7 is given by the expression

$$\alpha_\epsilon = \frac{w(\phi,1)}{\pi^2 R_L{}^3} \tag{3.1}$$

where $R_L = (Lb^2/6)^{1/2}$ is the radius of gyration of a tooth of the comb and $w(\phi,1)$ is a function of blend composition (ϕ is the volume fraction of the linear component 1) tabulated in ref 5. This function varies smoothly and monotonically from a value of 0.02933 at $\phi = 0$ to a value of 0.04563 at $\phi = 1$. It is also important to note that eq 3.1 is completely *universal* and independent of any monomer-scale cutoff. According to eq 2.8, bulk phase separation of the mixture is thus expected when $R_L{}^3$ is of order $V_<$, the smaller of the two molecular volumes, $V_1 = \nu N_1$ and $V_2 = 2\nu N_2$.

The excess free energy density for a homogeneous mixture of such components can again be written in the form of eq 2.3, but for the present linear−comb blend the cutoff proves unnecessary for the convergence of the integral:

$$\frac{\Delta F_E}{k_bT} = \frac{1}{4\pi^2}\int_0^\infty dk\, k^2 \ln\left[\frac{\phi S_1(k) + (1-\phi)S_2(k)}{S_1(k)^\phi S_2(k)^{1-\phi}}\right] \tag{3.2}$$

Because the dominant contribution to this integral occurs for wavevectors comparable to $R_L{}^{-1}$, the structure factors for two pure components can be simplified by taking N_1 and N_2 to infinity. Assuming Gaussian single-chain statistics, this leads to

$$S_1(k) = \frac{2}{k^2\beta^2} \tag{3.3}$$

where $\beta^2 \equiv b^2/(6\nu)$ and

$$S_2(k) = \nu L\{g(x_L) + [h(x_L)]^2 + 2x_L^{-1}h(x_L)[1 + \exp(-x_L)]\} \quad (3.4)$$

In the latter equation, we have used the shorthand $x_L \equiv (kR_L)^2$ and the functions $g(x)$ and $h(x)$ are Debye and Debye-like functions defined by

$$g(x) = 2x^{-2}[x + \exp(-x) - 1] \quad (3.5)$$

$$h(x) = [1 - \exp(-x)]/x \quad (3.6)$$

By rescaling the integral in eq 3.2, the excess free energy of a homogeneous mixture of linear and comb polymers can be written

$$\frac{\Delta F_E}{k_B T} = \frac{f_E(\phi)}{R_L^3} \quad (3.7)$$

where

$$f_E(\phi) = \frac{1}{4\pi^2}\int_0^\infty \mathrm{d}y\, y^2 \ln\left[\frac{2\phi/y^2 + (1-\phi)G(y^2)}{(2/y^2)^\phi G(y^2)^{1-\phi}}\right] \quad (3.8)$$

In this expression, $G(x)$ is a function defined by

$$G(x) = g(x) + [h(x)]^2 + 2x^{-1}h(x)[1 + \exp(-x)] \quad (3.9)$$

The integral in eq 3.8 is easily performed numerically. Figure 4a shows the ϕ dependence of f_E over the full composition range. The excess free energy is weakly asymmetric about $\phi = 1/2$; to highlight this fact, we have replotted the free energy as $f_E(\phi)/[\phi(1-\phi)]$ against ϕ in Figure 4b (solid points). The solid curve in this figure is a polynomial fit that is accurate to better than 1%:

$$f_E(\phi) \approx \phi(1-\phi)(0.003384 + 0.0003747\phi + 0.0001562\phi^2) \quad (3.10)$$

It should be noted that the sign of this compositional asymmetry is consistent with the form of f_E for short-branched blends; cf. eq 2.6. Again, we can summarize by stating that mixing a few linear chains into a branched melt ($\phi \to 0$) is energetically more favorable than mixing a few branched chains into a linear melt ($\phi \to 1$). As a final note, we comment that eq 3.1 can be derived by taking two derivatives of eq 3.7 with respect to composition (cf. eq 2.7).

Having discussed the free energy of a homogeneous mixture of linear and comb polymers, we now turn to the analysis of interfacial thermodynamics. In the subsequent discussion, we consider a flat interface between two strongly segregated phases. The bulk phase located at $z \to \infty$ is taken to be pure in component 1 (linear chains), while the phase at $z \to -\infty$ is assumed to be pure in comb polymers. From the above, it is clear that the strong segregation condition is easily met for mixtures in which $R_L^3 \ll V_<$, i.e., combs with frequent and proportionally short teeth.

By analogy with eq 2.9, a Cahn–Hilliard free energy functional for a flat interface between linear and comb polymers can be easily constructed:

$$\mathcal{F}[\phi] = \int_{-\infty}^{\infty} \mathrm{d}z \left\{R_L^{-3} f_E(\phi) + \left[\frac{\beta^2}{4\phi} + \frac{\beta^2}{8(1-\phi)}\right](\mathrm{d}\phi/\mathrm{d}z)^2\right\} \quad (3.11)$$

The first term on the right-hand side is again the local free energy penalty associated with compositions $\phi(z)$ differing from the coexistence values of zero and unity throughout the interfacial region. The square-gradient terms resemble those used for the short-branched blends (cf. eq 2.9), except that the term arising from the conformational entropy of the comb component is a factor of 1/2 smaller in eq 3.11. This extra factor of 1/2 is appropriate because the interfacial width ξ will subsequently be shown to greatly exceed R_L. Thus, in the random phase approximation analysis used to derive the square-gradient terms,[18] $S_2(k)$ should be evaluated in the regime $kR_L \ll 1$ rather than $kR_L \gg 1$, accounting for the factor of 1/2.

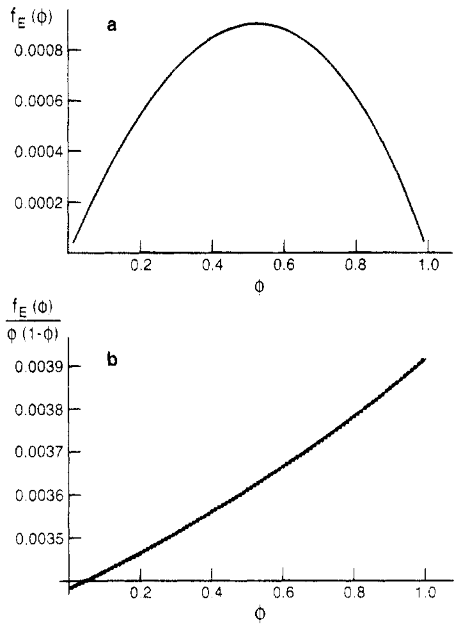

Figure 4. (a) Excess free energy function $f_E(\phi)$ for a mixture of chemically identical linear and comb polymers. (b) The compositional asymmetry of $f_E(\phi)$ is more clearly illustrated by plotting $f_E(\phi)/[\phi(1-\phi)]$ versus ϕ. The solid points denote results obtained by numerical integration of eq 3.8. The curve represents a polynomial fit to this numerical data: $f_E(\phi) \approx \phi(1-\phi)(0.003384 + 0.0003747\phi + 0.0001562\phi^2)$.

We can now repeat the analysis of $\mathcal{F}[\phi]$ outlined in the last section for the present case of a linear–comb interface. First, it proves convenient to rescale z according to $x = z/\xi$, where the *interfacial width* ξ is defined by

$$\xi \equiv \beta R_L^{3/2} \gg R_L \quad (3.12)$$

The latter inequality confirms our above claim about the interfacial width. With this spatial scaling, the minimizing composition profile is given implicitly by

$$\int_{1/2}^{\phi(x)} \mathrm{d}\phi\, [f_E(\phi)]^{-1/2}\left[\frac{1-\phi/2}{\phi(1-\phi)}\right]^{1/2} = 2x \quad (3.13)$$

The corresponding equilibrium interfacial tension is given explicitly by

$$\gamma/k_B T = \beta R_L^{-3/2}\int_0^1 \mathrm{d}\phi \left[\frac{1-\phi/2}{\phi(1-\phi)}\right]^{1/2}[f_E(\phi)]^{1/2} \approx 0.051762\beta R_L^{-3/2} \quad (3.14)$$

The above equations make it clear that the thermodynamic properties of interfaces between chemically identical linear and comb polymers are universal for all polymers with identical values of the measurables R_L

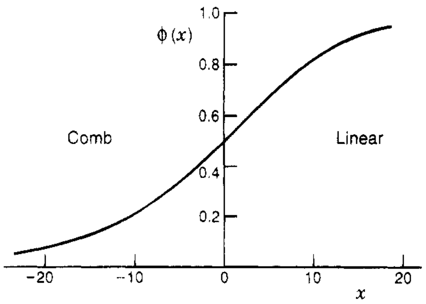

Figure 5. Composition profile $\phi(x)$ for a linear–comb blend obtained by numerical integration of eq 3.13. The spatial coordinate $x = z/\xi$ is scaled by a characteristic interfacial width ξ defined in eq 3.12.

and β. The composition profile that satisfies eq 3.13 is a universal function of the scaled variable x. In Figure 5, we show numerical results for this profile; the deeper penetration of linear chains into the branched phase is another manifestation of the asymmetry of $f_E(\phi)$ discussed above. Moreover, the universal form of the interfacial tension, $\gamma \sim k_BT\beta R_L^{-3/2}$, provides guidance in tailoring the tension of polymer–polymer interfaces of the type described here. The tension increases in proportion to β at fixed R_L; thus, e.g., polyethylene linear–comb interfaces would be expected to have a larger tension than polypropylene linear–comb interfaces at the same R_L. It is also apparent that the interfacial tension scales as $R_L^{-3/2}$ at fixed β; thus the tension can be decreased or increased by adjusting L according to $\gamma \sim L^{-3/4}$ (assuming L is long enough to permit the use of Gaussian statistics).

IV. Application to Polyolefin Block Copolymers

The results of the previous two sections, besides having obvious applicability to homopolymer interfaces, are also relevant to the *bulk* phase behavior of polyolefin block copolymers. Such materials have been studied extensively in the laboratory of F. S. Bates and have become standard model systems for exploring phase transitions[19] and rheology[20] in complex fluids. The most extensively studied systems are the diblock copolymers poly(ethylene–propylene)–poly(ethylethylene) (PEP–PEE) and polyethylene–poly(ethylethylene) (PE–PEE). However, Gehlsen and Bates[7] have recently reported on the synthesis and phase behavior of a large number of polyolefin diblock copolymers, including some with blocks of poly(vinylcyclohexane) (PVCH).

Bates and co-workers[1,7] have shown that in such polyolefin diblock copolymers a strong correlation exists between the value of the Flory–Huggins parameter χ deduced from measurements of the order–disorder transition temperature (ODT) and the difference in the β_i parameters (cf. eq 1.2) for the two blocks. Indeed the trends are in qualitative agreement with eq 1.1 (noting that $\chi = \nu\alpha_\epsilon$, where $\nu = (\nu_1\nu_2)^{1/2}$ is a mean segment volume). That eq 1.1 should be applicable to diblock copolymers, even though it was derived from homopolymer blends, is perfectly natural since the only composition fluctuations contributing to eq 1.1 are those with wavelengths intermediate between the monomer size and the radius of gyration scale. Thus, the connectivity of the blocks in a copolymer melt, relevant at the R_g scale, does not significantly influence the shorter-ranged fluctuation contributions to χ.

On the theoretical side, there have been a number of recent attempts to incorporate the effects of conformational and architectural asymmetry on the phase diagrams of block copolymers.[21-23] While these authors have properly accounted for the effects of conformational and architectural asymmetry on the *elastic* free energy of the block copolymer microphases, they have uniformly adopted the simple Flory–Huggins description of the excess free energy density, $f_E = \chi\phi(1 - \phi)$, to estimate the *interfacial* free energy contribution. Thus, χ (or the interfacial tension γ) and $\epsilon = (\beta_1/\beta_2)^2$ are considered to be *independent* parameters in these theories.

The arguments of the previous sections, however, suggest that χ (or γ) and ϵ *should not* be regarded as independent for polyolefin block copolymers. In such systems, sub-R_g composition fluctuations render χ a function of ϵ. Thus, a proper theoretical description of the weak segregation limit[19] of a polyolefin diblock copolymer melt should involve replacing χ by $\nu\alpha_\epsilon$, where α_ϵ is given as an explicit function of ϵ in eq 1.1. (For certain systems it may also prove necessary to include an enthalpic contribution to χ.) In theories for the so-called strong segregation limit,[19] where interfaces are narrow, the interfacial tension γ should be replaced by the ϵ-dependent expression given in eq 2.15. Thus, in both limits, conformational asymmetry should be incorporated into the interfacial as well as the elastic contributions to the free energy. While the phase boundaries between microphases are sensitive to this reinterpretation (i.e., ϵ dependence) of χ in the weak segregation limit, the free energies of all the microphases scale with the same power of the interfacial tension in the strong segregation limit. Thus, while phase boundaries are not shifted in the strong segregation limit by employing an ϵ-dependent γ, the microdomain spacings and free energy densities are. Finally, we note that the temperature dependence of such a theory for polyolefin block copolymers arises naturally through the temperature dependence of ϵ, which is well characterized.[1,12] A complication for quantitative analysis is that the cutoff Λ may also vary with temperature, although possibly in a predictable fashion.[24]

V. Summary

In the present paper we have demonstrated that the interfacial thermodynamic properties of nearly athermal polymer blends have certain universal characteristics. Specifically, we have shown that the interfacial composition profile can be expressed in a dimensionless form such that all polymer blends, when compared at the same values of certain measurable conformational and architectural parameters, have the same profile. The asymmetry of this profile reflects the tendency for linear chains to penetrate more deeply into phases rich in branched polymer chains than the reverse. Our results also provide insight into the conformational and architectural parameters that can be used to manipulate interfacial tension. Finally, we have shown how the present description of blend interfacial thermodynamics can be used to properly account for conformational asymmetry in the phase diagrams of polyolefin block copolymers.

Experimental tests of our findings would be extremely valuable, particularly in model linear–comb blends where numerical predictions can be made independent of any cutoff. For such tests, it may prove desirable to generalize our model to combs with teeth more closely spaced than L to maximize architectural asymmetry between linear and comb components and hence diminish enthalpic effects associated with coupling agents used to affix the teeth. Systematic studies of interfacial tension in linear–comb blends with varying numbers and lengths of teeth could be used to confirm the trends predicted herein.

Acknowledgment. This work was supported by the National Science Foundation under PYI Grant NSF-DMR 9057147 and by a Camille and Henry Dreyfus Teacher–Scholar Award. The author is grateful to F. S. Bates for stimulating discussions pertaining to this work.

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