Entropic Corrections to the Flory–Huggins Theory of Polymer Blends: Architectural and Conformational Effects

Glenn H. Fredrickson* and Andrea J. Liu

Departments of Chemical Engineering and Materials, University of California, Santa Barbara, California 93106

Frank S. Bates

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

Received November 22, 1993; Revised Manuscript Received February 7, 1994[●]

ABSTRACT: We compute fluctuation corrections to the Flory–Huggins theory for athermal or nearly athermal polymer mixtures. These excess free energy contributions arise from architectural and flexibility differences between components, are quasi-universal, and are generally positive, favoring demixing. Specific cases considered are binary blends of linear homopolymers, homopolymer/block copolymer mixtures, and blends of branched and linear homopolymers. We identify invariant parameters and mixing rules for such systems that may facilitate the design of miscible polyolefin blends.

I. Introduction

The Flory–Huggins theory[1,2] has proven to be an extremely versatile and convenient framework for describing the thermodynamic properties of molten polymer mixtures. This theory, which is a natural extension of regular solution theory for simple liquids, is based on the following expression for the free energy density of mixing of a binary system:

$$\frac{\Delta F}{k_B T} = \frac{\phi}{N_1 v_1} \ln \phi + \frac{1-\phi}{N_2 v_2} \ln(1-\phi) + \alpha\phi(1-\phi) \quad (1.1)$$

where ϕ is the volume fraction of component 1 and volume changes on mixing are neglected. The total molecular volume of the ith species, $N_i v_i$, has been decomposed into the volume of a statistical repeat unit, v_i, multiplied by the average number of segments per macromolecule, N_i. The first two terms in eq 1.1 represent the translational entropy of an ideal solution of macromolecules. The final term is an approximation for the excess free energy density of a binary mixture and was originally assumed to derive from purely enthalpic origins, namely, from differences in potential energy of close interactions between segments of the two species. It is common in the polymer literature to express the interaction energy density α in dimensionless form as a "Flory χ parameter" defined by[3,4]

$$\chi = \alpha(v_1 v_2)^{1/2} \quad (1.2)$$

although this procedure is unfortunate, because α is an invariant (independent of how statistical segments are defined),[3,4] while χ is not.

Equation 1.1, with α treated as a phenomenological and adjustable parameter, is capable of reproducing a large number of phase diagrams for binary polymer blends. However, significant composition dependence must often be ascribed to α. Moreover, the temperature dependence is usually not consistent with a purely enthalpic excess free energy; α can often be parameterized as $\alpha = A(\phi)/T + B(\phi)$. The second term in this expression indicates an entropic contribution to $\Delta F/k_B T$ that evidently depends on the *local* liquid structure, at and below the length scale of a statistical segment. Flory,[5] and later Sanchez and Lacombe,[6] suggested approximate but useful methods for incorporating local corrections to Flory–Huggins theory associated with finite compressibilities and thermal expansivities. In more recent years, Dudowicz and Freed[7] have developed systematic methods for correcting Flory–Huggins theory to include details of monomer shape and to better capture local monomer correlations. Recognizing that related issues of miscibility in simple liquid mixtures are best resolved in terms of continuum liquid state theories,[8] Schweizer and Curro[9,10] extended the highly successful reference interaction site model (RISM)[11] approach to polymer blends.

Except in close proximity to a critical consolute point, mixtures of simple molecular fluids rarely have density and composition correlations that persist over distances that exceed a few molecular diameters. Hence, in such systems the *local* liquid structure plays an integral role in determining the thermodynamics of mixing and we expect approximate parameterizations such as α to be highly dependent on the details of molecular shapes and sizes. In *polymer blends*, however, due to the intramolecular connectivity, there naturally exist correlations in species density over a range of length scales between the monomer size and the radius of gyration. (Near a critical point, even longer ranged correlations are possible.) Indeed, the correlation hole effect[12] is a direct and measurable consequence of this *nonlocal* liquid structure, i.e., segment density correlations on scales that can greatly exceed the segment length or monomer size. Although this point is generally not appreciated, there may also be significant contributions to the excess free energy of polymer mixtures associated with such nonlocal liquid structure. The polymer RISM approach[9,10] naturally incorporates these contributions due to its simultaneous treatment of intra- and intermolecular correlations. Indeed, predictions[9,10] of an N_i dependence of α under certain conditions is a manifestation of nonlocal correlation effects. The lattice approach of Dudowicz and Freed may also be capable of including such longer ranged correlations, although to our knowledge this has not been explicitly demonstrated.

Contributions to the excess free energy (or α) for polymer mixtures arising from nonlocal correlations are of great interest because they may possess partial or complete *universality*. Complete universality would imply, for

---

[●] Abstract published in *Advance ACS Abstracts*, March 15, 1994.

0024-9297/94/2227-2503$04.50/0

example, that all polymer mixtures, when prepared with the same values of measurables such as radii of gyration and with identical architectures, would have have identical values of α independent of the chemical details of the monomers employed. Partial universality might imply that a contribution to the excess free energy could be factored into a part with complete universality and a second part that depends on the local liquid structure. As we shall see below, even such partial (or quasi) universality can have important implications for the design of miscible polymer blends.

While nonlocal contributions to the excess free energy can in principle be studied by computer simulation methods or numerical approaches, such as RISM, it is often the case that universal or quasi-universal contributions can be more easily extracted by using field-theoretic methods that coarse-grain or smooth out chemical details below the statistical segment length scale. These methods have the virtue that simple *analytical* expressions can often be obtained. In a recent communication,[13] we reported on the results of such a calculation for an athermal binary blend of homopolymers with unequal statistical segment lengths. We found a nonlocal contribution to α for this system arising from correlated composition fluctuations on *intermediate* length scales between the segment scale and the radius-of-gyration scale. Although the result exhibits only partial universality in the sense described above, it does suggest a combination of invariant pure-component parameters that should be closely matched for the two components in order to promote miscibility. To our knowledge, these parameters have not been previously associated or correlated with polymer–polymer miscibility, and it is our belief that this recognition could have profound commerical implications.

In the present paper, we provide the derivation of the result announced in this recent communication and extend the approach to mixtures of components that differ in architecture as well as in conformational properties. We also discuss mixtures of copolymers and homopolymers, but to simplify the analysis, we restrict consideration to *athermal* blends in which the enthalpic contribution to α is either identically zero or negligible compared to the entropic contributions identified below. It appears that a number of important polyolefin mixtures may fall in this category.[14,15] Finally, we note that Olmsted and Milner[16] have recently followed a similar approach to explore the role of block size on the miscibility of block copolymers and homopolymers, although in their study the segment lengths and volumes were precisely matched so that the conformational asymmetry effects identified below vanish identically. Also closely related is some recent analytical work by Schweizer[17] on a new closure scheme for the polymer RISM equations. Although he did not consider mixtures of architecturally different polymers, his results for conformationally asymmetric athermal blends appear to be similar and complementary to our findings in section III.A.

II. Free Energy of an Athermal Binary Blend

A. General Approach. In the present section we outline a theoretical approach to computing excess contributions to the free energy density for a general binary mixture of athermal polymers. The two components under consideration, which will be labeled 1 and 2, could be homopolymers, either branched or linear, or copolymers of arbitrary sequence distribution and architecture. Our primary restriction is that the various branches, or blocks in the case of copolymers, must be long enough for Gaussian statistics to apply in the pure component melt. Thus, our analysis may not apply to certain copolymers that lie intermediate to block (or graft) and random architectures. The binary melt is further assumed to be athermal and the *local* liquid structure is ignored in our model and replaced by a constraint of local incompressibility. In a canonical ensemble in which a total of $n_1 + n_2$ chains fully occupy a volume V, the configurational partition function can thus be written as

$$Z = \frac{1}{n_1!n_2!}\int \mathcal{D}\mathbf{R}\,\exp[-H_0(\mathbf{R})/k_\mathrm{B}T] \prod_{\mathbf{k}\neq 0} \delta[\hat{\phi}_1(\mathbf{k}) + \hat{\phi}_2(\mathbf{k})] \tag{2.1}$$

where $\int\mathcal{D}\mathbf{R}$ denotes integration over the positions of all statistical segments of each species and $H_0(\mathbf{R})$ is a Hamiltonian for a collection of $n_1 + n_2$ noninteracting chains of the two species. We assume Gaussian statistics for the pure components, so that for example in the case of a blend of two linear homopolymers, H_0 is given by

$$H_0(\mathbf{R})/k_\mathrm{B}T = \frac{3}{2{b_1}^2}\sum_{j=1}^{n_1}\int_0^{N_1}\mathrm{d}s\left(\frac{\mathrm{d}\mathbf{R}_j}{\mathrm{d}s}\right)^2 + \frac{3}{2{b_2}^2}\sum_{j=1}^{n_2}\int_0^{N_2}\mathrm{d}s\left(\frac{\mathrm{d}\mathbf{R}_j}{\mathrm{d}s}\right)^2 \tag{2.2}$$

where b_1,b_2 and N_1,N_2 denote the statistical segment lengths and numbers of statistical segments per chain, respectively, of the two *pure* components. The notation $\mathbf{R}_i(s)$ is used to represent the spatial position of the sth statistical segment on the ith chain. Similar expressions can be easily written for copolymers or branched molecules. The only interactions between chains included in eq 2.1 are due to the last factor, which incorporates the constraint of local incompressibility. The quantity $\hat{\phi}_i(\mathbf{k})$ is the **k**th Fourier coefficient of the microscopic volume fraction of species i (i = 1 or 2) and has explicit dependence on the configuration of the segments, **R**. Again, precise expressions depend on the system of interest, but for example in the case of linear homopolymers $\hat{\phi}_i$ is given by

$$\hat{\phi}_i(\mathbf{k}) = v_i \sum_{j=1}^{n_i}\int_0^{N_i}\mathrm{d}s\,\exp[i\mathbf{k}\cdot\mathbf{R}_j(s)] \tag{2.3}$$

where v_i denotes the volume of a type i statistical segment. It should be emphasized that the $\mathbf{k} = 0$ component is excluded from the product in eq 2.1 because the $\mathbf{k} \rightarrow 0$ limit of eq 2.3 is proportional to the overall volume fraction of species i, which does not fluctuate in the canonical ensemble.

Our analysis of eq 2.1 proceeds with the replacement of the terminal product of δ functions by a functional integral over a conjugate field J with Fourier components $J(\mathbf{k})$. This leads to the expression

$$Z = Z_0\int \mathcal{D}J\,\exp[n_1G_1(J) + n_2G_2(J)] \tag{2.4}$$

where Z_0 is the partition function for the noninteracting system

$$Z_0 = \frac{1}{n_1!n_2!}{Z_1}^{n_1}{Z_2}^{n_2} \tag{2.5}$$

and the functional $G_j(J)$ (j = 1 or 2) is defined by

$$G_j(J) = \ln\langle \exp[iV^{-1}\sum_{\mathbf{k}\neq 0} J(-\mathbf{k})\hat{\phi}_j(\mathbf{k})]\rangle_0 \qquad (2.6)$$

with $i = \sqrt{-1}$. On the right-hand side of eq 2.5, Z_j denotes the noninteracting, partition function of a *single* type j chain, i.e., $\int \mathcal{D}\mathbf{R} \exp[-H_0(\mathbf{R})/k_BT]$. Similarly, the average denoted by $\langle \dots \rangle_0$ on the right-hand side of eq 2.6 represents a *single-chain* average with Boltzmann weight $\exp[-H_0(\mathbf{R})/k_BT]$, and $\hat{\phi}_j(\mathbf{k})$ in that expression is to be interpreted as the contribution of a *single chain* of type j to the total $\hat{\phi}_j$, given for example by an expression like eq 2.3.

Equation 2.4 is a representation for the partition function of our model binary polymer melt that naturally separates ideal and nonideal (excess) contributions to the free energy of mixing. The Helmholtz free energy arising from the first factor,

$$F_0 = -k_BT \ln Z_0 \qquad (2.7)$$

after separation of terms linear in the volume fractions of the two species and division by the total volume, exactly reproduces the first two (ideal) terms in the Flory–Huggins expression eq 1.1. The logarithm of the second factor in eq 2.4 (involving the functional integral over the chemical-potential-like field J) thus represents the excess contribution to the free energy. Because we have assumed an athermal blend, this excess contribution is purely entropic in origin, when expressed in the form of the last term of eq 1.1., corresponds to a temperature-independent, but composition-dependent interaction parameter α. (In practice, we note that the pure component parameters b_i and v_i are found to vary with temperature, so our expressions for α will acquire a T-dependence when experimentally determined values of these parameters are employed.)

The functional integral over $\{J(\mathrm{k})\}$ in eq 2.4 unfortunately cannot be performed exactly. Moreover, the field theory is actually ill-defined because the integrand of eq 2.4 does not sufficiently penalize fluctuations in Fourier coefficients of the J field with very large values of $k = |\mathbf{k}|$. This deficiency is due to our neglect of the local liquid structure and is critical for fluctuations with wavenumbers k that exceed the reciprocal of the segment size. Fortunately, we can cure the problem (i.e., eliminate divergences) by simply introducing a large-k cutoff into all sums or integrals over $\mathbf{k}$ that emerge from the theory. However, it should be noted that all free energy contributions that ultimately depend on the value of the cutoff, and hence on the local liquid structure, are at best only quasi-universal.

B. Gaussian Approximation. The functional $G_j(J)$ that enters the integrand of eq 2.4 has a quite complicated dependence on J but can in principle be computed systematically in powers of J by evaluating multipoint correlation functions of single-chain density.[18,19] In the present paper we restrict consideration to the simplest possible approximation for the integral in eq 2.4, which results by truncating the expansion of $G_j(J)$ at second order in J. The resulting integral is therefore Gaussian and can be performed analytically. A similar approximation for polymer solutions is discussed in section 5.2 of the text by Doi and Edwards.[19]

It appears to be very difficult to rigorously justify the Gaussian approximation for the most general type of binary blend treated here. Indeed, the field theory defined above, when applied to the blend of linear homopolymers considered in section III.A, is particularly ill-behaved and higher order free energy contributions (so-called "loop" corrections) are apparently of the same order as the Gaussian corrections retained here.[20] Nevertheless, the Gaussian approximation yields physically reasonable answers, gives corrections to Flory–Huggins theory that are arbitrarily small as conformational and architectural differences between components vanish, and identifies some very useful invariant combinations of parameters that control miscibility. Moreover, for the linear/branched blends treated in sections III.C. and III.D, the Gaussian approximation is apparently the first of a series of systematic approximations and provides the leading-order excess free energy contribution for low densities of branch points. Thus, in the present paper we explore the implications of the Gaussian approximation without concerning ourselves with its justification. The latter will be deferred to future work.

Invoking the Gaussian approximation, the functional integral in eq 2.4 can be reduced to

$$Z = Z_0 \int \mathcal{D}J \exp[-1/(2V) \sum_{\mathbf{k}\neq 0} J(\mathbf{k})\, J(-\mathbf{k})(\phi_1 S_1(k) + \phi_2 S_2(k))] \qquad (2.8)$$

where $S_j(k)$ is proportional to the structure factor of a noninteracting type j chain:

$$S_j(k) = \frac{1}{V_j}\langle \hat{\phi}_j(\mathbf{k})\, \hat{\phi}_j(-\mathbf{k})\rangle_0 \qquad (2.9)$$

In the above equations, V_j denotes the total volume of a type j molecule and $\phi_j = n_jV_j/V$ is the average volume fraction occupied by species j. Because of our assumption of incompressibility, $\phi_2 = 1 - \phi_1$. The final step is simply to perform the Gaussian integral over J and take minus the logarithm of the result. This gives an excess free energy density that can be written compactly in the thermodynamic limit as

$$F^{\mathrm{E}}/k_BT = \frac{1}{2(2\pi)^3}\int \mathrm{d}\mathbf{k}\, \ln[\phi_1 S_1(k) + \phi_2 S_2(k)] \qquad (2.10)$$

where we have disregarded terms linear in ϕ_1. The total free energy density of mixing in the Gaussian approximation is thus

$$\Delta F/k_BT = \frac{\phi_1}{V_1}\ln \phi_1 + \frac{\phi_2}{V_2}\ln \phi_2 + F^{\mathrm{E}}/k_BT \qquad (2.11)$$

Finally, because we will be particularly interested in studying the spinodal curves predicted by eq 2.11, it is convenient to give a special name to the second derivative of F^{E} with respect to $\phi \equiv \phi_1$:

$$\alpha_\epsilon \equiv -\frac{1}{2k_BT}\frac{\partial^2 F^{\mathrm{E}}}{\partial \phi^2} = \frac{1}{8\pi^2}\int_0^{\Lambda_b} \mathrm{d}k\, k^2 \left[\frac{S_1(k) - S_2(k)}{\phi S_1(k) + (1-\phi)S_2(k)}\right]^2 \qquad (2.12)$$

In this equation we have incorporated a high-k cutoff at a value $\Lambda_b \sim (b_1b_2)^{-1/2}$ as discussed above. Moreover, we have chosen the symbol α_ϵ for the second derivative of F^{E} because it plays the same role in the spinodal equation as the interaction density α in the Flory–Huggins theory (cf. eq 1.1), so in this sense can be thought of as an entropic contribution to the interaction density or χ parameter. Nevertheless, α_ϵ is composition dependent and thus confusion may arise unless one keeps the definition eq 2.12 in mind. In particular, an effective interaction density might be defined by comparing the last terms in eqs 1.1 and 2.11: $\alpha_{eff} = F^{\mathrm{E}}/[k_BT\phi(1-\phi)]$. Finally, we note that with the above definition, the spinodal equation ($\partial^2\Delta F/\partial\phi^2 = 0$) can be written simply as

$$\frac{1}{V_1\phi} + \frac{1}{V_2(1-\phi)} - 2\alpha_\epsilon = 0 \tag{2.13}$$

III. Applications

A. Binary Blends of Linear Homopolymers. As a first application of the Gaussian approximation outlined above, we reproduce the expression for α_ϵ reported previously by Bates and Fredrickson for a binary mixture of two homopolymers.[13] Specifically, we consider a blend of type A homopolymers, each chain consisting of N_A statistical segments of segment length b_A, with type B homopolymers, each with N_B segments of length b_B. The molecular volumes of the two species can be expressed as $V_i = N_i v_i$ (i = A or B). The structure factors for a single chain of the two pure components are well-known[12] and can be expressed as

$$S_i(k) = N_i v_i g(x_i) \tag{3.1}$$

where $x_i \equiv (kR_i)^2$ and $R_i^2 = N_i b_i^2/6$ denotes the mean squared radius of gyration of species i. The function $g(x)$ is the familiar Debye function

$$g(x) = 2x^{-2}[x + \exp(-x) - 1] \tag{3.2}$$

which has the limiting behaviors $g(x) \approx 2/x - 2/x^2$ for $x \gg 1$ and $g(x) \approx 1 - x/3$ for $x \ll 1$.

Substitution of eq 3.1 into eq 2.12 leads to an integral over k that can be broken into two intervals, $(0, \Lambda_R)$ and (Λ_R, Λ_b), where Λ_R is a wavenumber that is of order the reciprocal of the smaller of the two pure component radii of gyration. Unless the conformational properties of the two species are extremely closely matched (as defined below), it is generally the case that the contribution to the integral from the second interval, which is of order Λ_b^3, greatly exceeds the contribution from the first interval, which is $\mathcal{O}(\Lambda_R^3)$. Inserting the asymptotic form $g(x_i) \approx 2/x_i$ into eq 2.12, it follows that α_ϵ is given approximately by

$$\alpha_\epsilon = \frac{\Lambda_b^3}{24\pi^2}\left[\frac{1-(\beta_A/\beta_B)^2}{\phi + (1-\phi)(\beta_A/\beta_B)^2}\right]^2 \tag{3.3}$$

where

$$\beta_i^2 \equiv \frac{b_i^2}{6v_i} \tag{3.4}$$

are the invariant (independent of segment definition) parameters introduced by Helfand and Sapse.[3]

Equation 3.3, because of the dependence of the factor Λ_b^3 on *local* liquid structure and hence on the chemical details of the segments, is only quasi-universal. Nevertheless, the second factor in eq 3.3 is *universal* for all homopolymer blends with the same ratio of β's and average volume fraction $\phi = \phi_A$. Thus, an obvious path to identifying miscible polymer blends (in the absence of specific interactions) would be to find components for which

$$\epsilon \equiv (\beta_A/\beta_B)^2 \tag{3.5}$$

is as close to unity as possible, thereby minimizing the second factor in eq 3.3. Indeed, Bates et al.[14] have demonstrated that this approach can successfully correlate the experimental phase behavior of a number of polyolefin mixtures and block copolymers. The beauty of this method is due to the simplicity of eq 3.3 and the fact that the "conformational asymmetry" ratio ϵ depends only on *pure component* determinations of radii of gyration and molecular volumes (note that β_i^2 can be expressed as R_i^2/V_i).

A few more comments regarding eq 3.3 are in order. First of all, we note that the parameters β_i would seem to be local quantities, because they define lengths that are of order the segment size. However, these parameters arose naturally by summing the contributions of chemical potential (i.e., J) fluctuations to the free energy density on a broad range of length scales between the segment size and the radius of gyration. Thus, they truly reflect nonlocal packing and conformational effects; the universality of the second factor in eq 3.3 is indeed a consequence of this nonlocality. A second point is that the β_i parameters emerge from theories of *nonuniform* systems, like the asymmetric polymer–polymer interfaces studied by Helfand and Sapse,[3] at the *mean field* level of calculation. In the present case of a uniform, homogeneous blend, an assessment of fluctuation corrections to mean field theory (Flory–Huggins) was required to uncover the β_i dependence of the excess free energy. Another important prediction made by eq 3.3 is the explicit composition dependence of α_ϵ, which influences the spinodal though eq 2.13. If $\epsilon = (\beta_A/\beta_B)^2 > 1$, implying that component A is conformationally more extended in pure form than B, then α_ϵ is a monotonically increasing function of the volume fraction of A, $\phi = \phi_A$. This implies that adding a small amount of a low-β component to a high-β melt is less likely to lead to miscibility than the addition of a small amount of a high-β component to a low-β melt. Indeed, such asymmetry in phase behavior has been observed in one of our laboratories for several different polyolefin blends.[21] Finally, we note that expressions similar to eq 3.3 have been recently derived by Schweizer[17] on the basis of a new closure scheme for the polymer RISM equations. Although the relationship between the present approach and Schweizer's more ambitious study will require further investigation, it is evident that they provide complementary information on the quasi-universality of conformational asymmetry effects in polymer blends.

In practice, eq 3.3 must be used cautiously since α may contain additional local excess free energy contributions as described earlier.[13] Moreover, the usual parameterization $\alpha = A(\phi)/T + B(\phi)$, which ascribes entropic excess free energy to $B(\phi)$, will not properly account for the temperature dependence of the β_i's. For most hydrocarbon polymer melts,[14,22] $\partial \ln v_i/\partial T \approx 6.5(\pm 1.5) \times 10^{-4}$, leading to a 5–8% increase in segment volume per 100 degrees centigrade of temperature elevation. In contrast, the thermal expansion factor for the polymer coil dimensions can be either positive or negative;[22] representative values are $\partial \ln R_{PE}/\partial T = -0.6 \times 10^{-3}$, $\partial \ln R_{PEP}/\partial T = -0.6 \times 10^{-3}$, and $\partial \ln R_{PEE}/\partial T = 2.0 \times 10^{-3}$, where PE, PEP, and PEE denote poly(ethylene), poly(ethylenepropylene), and poly(ethylethylene), respectively. Thus, β may have significant and interesting temperature dependence; $\partial \ln \beta_{PE}/\partial T \approx -1.8 \times 10^{-3}$, $\partial \ln \beta_{PEP}/\partial T \approx -1.8 \times 10^{-3}$, and $\partial \ln \beta_{PEE}/\partial T \approx -0.4 \times 10^{-3}$.

A particularly interesting aspect of this thermal effect is that α_ϵ may either decrease *or* increase with temperature. For example, if $\beta_A > \beta_B$, but $\partial \ln \beta_A/\partial T < \partial \ln \beta_B/\partial T$, then increasing temperature would initially decrease α_ϵ. However, if β_A and β_B are sufficiently closely matched to begin with, then after reaching the ideal mixing condition ($\epsilon = 1$), further increases in temperature will *lower* the miscibility since $(1-\epsilon)$ in eq 3.3 will change sign. This implies that we can anticipate lower critical solution temperature (LCST) behavior for certain combinations of nonpolar hydrocarbon polymers, a result that runs counter to classical arguments.

B. Binary Mixtures of Homopolymers and Copolymers. On the basis of the above results for a blend of two homopolymers, a very promising scheme for designing miscible blends (in athermal, or nearly athermal, systems, e.g., polyolefins) would be to try to design a copolymer whose "mean" β closely matches the β of some homopolymer of interest. In fact, this approach has been successfully implemented in the literature.[14] However, the appropriate "mean" to employ in such applications is not obvious. An important application of the present theory is thus to establish the appropriate (hopefully universal) mixing rules necessary to compute an effective value of β for a copolymer component.

To begin our analysis, we consider a binary mixture of a type A linear homopolymer (N_A segments of length b_A) with a B–C diblock copolymer (N_B segments of length b_B linearly connected to N_C segments of length b_C). For the purpose of applying the formulas of section II, we will subsequently refer to the homopolymer as species 1 and the copolymer as species 2. The statistical segment volumes of the three types of segments will be denoted by v_A, v_B, and v_C. It also proves convenient to define a compositional parameter for the diblock species, namely, the volume fraction of type B segments:

$$f = N_B v_B/(N_B v_B + N_C v_C) \tag{3.6}$$

With these definitions, we simply require the scattering functions of eq 2.9 for each component. For the homopolymer component 1, the appropriate expression is again given by eq 3.1. For a diblock copolymer, the scattering function $S_2(k)$ has been worked out by Leibler.[18] (Actually, we have generalized Leibler's result to allow for unequal segment lengths and volumes.) As in the previous section, however, only the intermediate k asymptotic behavior of the two scattering functions is required to extract the leading-order contribution to α_ϵ. [The corrections are smaller by $(\Lambda_R/\Lambda_b)^3$ with the scale of Λ_R^{-1} determined by the smallest of the three radii of gyration, R_A, R_B, and R_C.] We find the simple result that at intermediate k, i.e., $\Lambda_R < k < \Lambda_b$, both structure factors can be written in the form

$$S_i(k) \approx 2(k\beta_i)^{-2} \tag{3.7}$$

where $\beta_1 = \beta_A$ for the type A homopolymer and the *effective* β for the B–C copolymer component is given by

$$\beta_2^{-2} = f\beta_B^{-2} + (1-f)\beta_C^{-2} \tag{3.8}$$

Thus, the appropriate "mean" β parameter for a diblock copolymer component is not a simple volume fraction weighted arithmetic mean of β_B and β_C, but is given by the more complicated expression in eq 3.8. The corresponding expression for the "entropic" interaction density α_ϵ of the homopolymer/diblock blend is strictly analogous to eq 3.3:

$$\alpha_\epsilon = \frac{\Lambda_b^3}{24\pi^2}\left[\frac{1-(\beta_1/\beta_2)^2}{\phi + (1-\phi)(\beta_1/\beta_2)^2}\right]^2 \tag{3.9}$$

where $\phi = \phi_1$ is the volume fraction of homopolymer.

It turns out that eqs 3.8 and 3.9 have more general applicability than to just homopolymer/diblock copolymer blends. If we extend the above analysis to binary mixtures of type A homopolymers with other types of B–C block copolymers, e.g., triblock or multiblock copolymers, we find precisely the same expressions for the effective copolymer β and for α_ϵ as given above. This follows because the scattering function of a B–C block copolymer in the intermediate k regime (i.e., length scales between the segment size and the smallest block size) is independent of the sequence distribution, degree of polydispersity, and architectural arrangement of the B and C blocks. In this regime, which provides the dominant contribution to α_ϵ, only the copolymer composition f is relevant and the effective β for the copolymer is given in terms of pure component β's by eq 3.8, *regardless of architecture*.

The above conclusions continue to hold until the mean block size becomes so small that Gaussian statistics no longer apply for individual blocks within the pure copolymer melt or until the corrections to eq 3.9 become significant, i.e., when Λ_R/Λ_b becomes $\mathcal{O}(1)$ with the scale of Λ_R^{-1} set by the mean of the block size distribution function. Thus, eqs 3.8 and 3.9 would not be expected to hold for "ideal" statistical copolymers; in such cases the effective value of β can generally *not* be expressed as a universal function of the pure component β's and should be determined by experimental measurement of R_2 and V_2.

For statistical copolymers that are "ideal" or that have a tendency for alternation, and in spite of the fact that universality is not expected, a different mixing rule for β is probably more accurate than eq 3.8. If, for example, we model the copolymer component as a freely jointed chain with randomly distributed links of fixed lengths b_A and b_B, then it is easy to demonstrate that

$$\beta_2^2 = R_2^2/V_2 = f\beta_B^2 + (1-f)\beta_C^2 \tag{3.10}$$

This expression is a good starting point for trying to design a random copolymer with an effective value of β that would closely match the β value of a second component. Indeed, experimental results obtained previously[14] for a mixture of PEP with a model PE–PEE random copolymer are in quantitative agreement with eq 3.10.

C. Blends of Chemically Identical Linear and Star Homopolymers. In the previous two sections we have investigated entropic corrections to Flory–Huggins theory associated with *conformational asymmetry effects*, i.e., due to a mismatch in the backbone flexibilities and packing characteristics of the two types of chains. However, our Gaussian approximation for the free energy of mixing, summarized by eqs 2.10–2.12, also predicts entropic corrections associated solely with *architectural asymmetry* between components. To investigate such effects, we have analyzed two idealized types of binary homopolymer mixtures: a blend of linear and p-arm star homopolymers composed of identical monomers, and a blend of linear and branched (chemically identical) homopolymers with the architecture depicted in Figure 1b.

In the present section, we discuss the linear/star blend shown in Figure 1a. Component 1 is a linear homopolymer consisting of N_1 statistical segments, each of length b and volume v. Component 2 is a star homopolymer of the same chemical constitution and has p arms with equal numbers of segments, N_2. The segment length b and volume v are taken to be the same as for component 1. The molecular volumes of single molecules of the two components are thus given by $V_1 = N_1 v$ and $V_2 = pN_2 v$. To evaluate the excess free energy density or α_ϵ in the Gaussian approximation, we again require the single-chain structure factors of the two pure components. For component 1, we have from eq 3.1

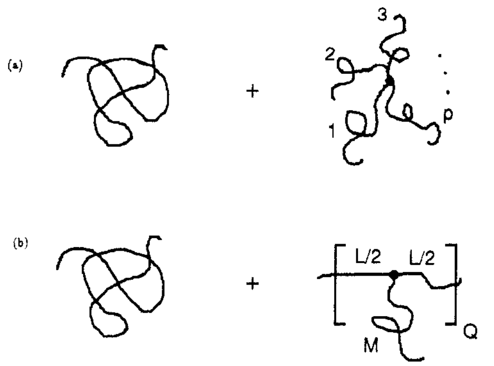

Figure 1. Schematic of the architecturally asymmetric blends considered in the present paper. (a) A linear/star blend. Component 1 is a linear homopolymer, consisting of N_1 statistical segments, each of length b and volume v. Component 2 is a p-arm star homopolymer, constructed from the same monomers as component 1, with N_2 statistical segments per arm. (b) A linear/branched blend. Component 1 is the same linear homopolymer as in (a). Component 2 is a graft polymer, again constructed from the same type of monomer, with M statistical segments per graft and L statistical segments between grafts. The total number of repeated units of volume $v(L + M)$ is denoted by Q.

$$S_1(k) = N_1 v g(x_1) \qquad (3.11)$$

where $g(x)$ is the Debye function of eq 3.2 and $x_i \equiv (kR_i)^2$ with $R_i^2 = N_i b^2/6$ as before. For the star homopolymer component it is a simple matter to work out the corresponding scattering function,[23] assuming Gaussian statistics for each arm:

$$S_2(k) = N_2 v[g(x_2) + (p-1)h^2(x_2)] \qquad (3.12)$$

In this expression, $h(x)$ is a second Debye-like function defined by

$$h(x) = x^{-1}[1 - \exp(-x)] \qquad (3.13)$$

When the above expressions for $S_i(k)$ are substituted into eq 2.10 or 2.12, the contributions from various intervals of the k integration can be investigated independently. Provided that $p \gg 1$, it is possible to show that the dominant contribution to the k integrals comes from the interval (Λ, Λ_b), where Λ^{-1} is a length scale determined by the smallest of R_1 (linear homopolymer radius of gyration) and R_2 (star arm radius of gyration). In this interval, the $S_i(k)$ can be approximated by asymptotic expressions for large k; however, it proves necessary to retain terms of order k^{-4} as well as the leading-order k^{-2} terms. Substitution of these approximate expressions into eq 2.12 for α_ϵ yields the following integral:

$$\alpha_\epsilon \approx \frac{[2 + (p-3)(R_1/R_2)^2]^2}{8\pi^2} \times \int_\Lambda^{\Lambda_b} \mathrm{d}k \frac{k^2}{[2(R_1 k)^2 - 2\phi + (1-\phi)(p-3)(R_1/R_2)^2]^2} \qquad (3.14)$$

This integral, however, converges for $\Lambda_b \to \infty$, so we can safely extend the upper limit to infinity. On rescaling, the resulting integral can be written

$$\alpha_\epsilon \approx \frac{[2 + (p-3)(R_1/R_2)^2]^2}{8\pi^2 (2R_1^2)^{3/2}[(1-\phi)(p-3)(R_1/R_2)^2 - 2\phi]^{1/2}} \times \int_{x_0}^{\infty} \mathrm{d}x \frac{x^2}{(1+x^2)^2} \qquad (3.15)$$

where

$$x_0 \equiv \left[\frac{2R_1^2\Lambda^2}{(1-\phi)(p-3)(R_1/R_2)^2 - 2\phi}\right]^{1/2} \qquad (3.16)$$

Evidently, the largest contribution to α_ϵ is possible when $(p-3)(R_1/R_2)^2 \gg 1$, i.e., for large numbers of short arms or large homopolymers. When this condition is met (except at compositions extremely close to $\phi = 1$), we can set $x_0 \to 0$ in the lower limit of integration and reduce eq 3.15 to the *universal* form

$$\alpha_\epsilon \approx \frac{1}{64\pi\sqrt{2}} \frac{(p-3)^{3/2}}{(1-\phi)^{1/2} R_2^3} \qquad (3.17)$$

From this expression it is clear that the entropic contribution to the interaction density for a linear/star blend grows (for large p) as the $^3/_2$ power of the number of arms of the star and is inversely proportional to the cube of the arm radius of gyration.

Next, we consider the implications of eq 3.17 for phase separation of our model linear/star blend. For the present purposes, it will prove sufficient to analyze the spinodal equation, eq 2.13. By combining eqs 2.13 and 3.17, the condition for the stability limit of the homogeneous phase of a linear/star blend can be written in dimensionless form as

$$\frac{1}{\phi} + \frac{1}{(V_2/V_1)(1-\phi)} - \frac{1}{32\pi\sqrt{2}} \frac{(p-3)^{3/2}}{(1-\phi)^{1/2}} \frac{V_1}{R_2^3} = 0 \qquad (3.18)$$

where the V_i denote the *total* molecular volumes of a chain of each species as before. The first two terms in this expression represent the ideal solution entropy of mixing and are evidently smallest, i.e., $\mathcal{O}(1)$, when $V_2/V_1 \geq 1$. The last term on the left-hand side of eq 3.18 (the excess contribution) thus must be of order unity for phase separation to occur. Formally, this term scales as $(p - 3)^{3/2}N_1 N_2^{-3/2}(v/b_3)$, although it is multiplied by a numerically small coefficient, $3\sqrt{3}/(16\pi) \approx 0.1034$. As a practical matter, it is difficult to synthesize well-defined star polymers with more than ~20 arms and, for the present theory to apply, each arm must be long enough to be Gaussian, requiring $N_2 \geq 10$. Thus, the factor $[(p-3)/N_2]^{3/2}$ is at best of order unity. It is also generally the case that v/b^3 is significantly smaller than unity, often of order 10^{-1}–10^{-2}. Maintaining $N_1 \approx pN_2$, so that $V_2/V_1 \approx 1$, we therefore conclude that phase separation may be possible for p = 10–15 arm stars of arm length $N_2 \approx 10$, mixed with a $N_1 \approx 100$ linear homopolymer. This is of course an extreme situation and depends sensitively on v/b^3 not being too small for the material selected.

For more conventional mixtures of linear and star polymers with modest numbers of truly polymeric ($N_2 > 100$) arms, the above considerations suggest that phase separation due to architectural differences alone is unlikely. Nevertheless, there may be a signature of the nonideal thermodynamics described by eq 3.17 in the one-phase region of such blends that is manifested, for example, in scattering measurements. In particular, the compositional asymmetry of eq 3.17 is pronounced, as in the case of linear blends. It is apparent that addition of a low concentration of stars to a linear melt is less favorable thermodynamically than addition of a low concentration of linear chains to a star melt.

We are not aware of published experiments dealing with the thermodynamics of linear and star homopolymer mixtures composed of a single type of repeat unit.

However, there have been at least two reports describing the phase behavior of linear poly(vinyl methyl ether) (PVME) and star polystyrene (PS) with[25] $p = 4$ and $p = 22$.[24] In both cases the effects of the star architecture on the phase diagram were small, in qualitative agreement with our calculations.

D. Blends of Chemically Identical Linear and Branched Homopolymers. From the above arguments leading to eq 3.17, it is apparent that the value of α_ϵ in the case of a linear/star homopolymer mixture is limited by the fact that there is only *one* branch point per star molecule and by synthetic constraints that restrict p to be less than ~ 20. A way to increase the nonideality of a mixture of linear and branched, but otherwise identical polymers is evidently to increase the concentration of branch points on each branched macromolecule. To explore this effect, we have studied a second athermal mixture of chemically identical chains in which the linear species is again a homopolymer of molecular volume $V_1 = vN_1$, but the branched species 2 has the architecture shown in Figure 1b. The graft (comb) architecture of the second component has grafts of M statistical segments, spaced evenly along the linear backbone every L statistical segments. The periodically repeated unit, with molecular volume $v(L + M)$, is repeated Q times, for a total molecular volume per polymer of $V_2 = vQ(L + M)$. Of primary interest will be cases of short, but frequent branches, such that the following conditions are satisfied: $1 \ll L, M \ll QL, N_1$. We note that the left inequality is required to ensure Gaussian chain statistics.

As before, we proceed in our analysis by determining expressions for the single-molecule structure factors of both species. For the homopolymer, the required expression for $S_1(k)$ is again given by eq 3.11. It is relatively straightforward to derive an expression for the structure factor of the graft polymer depicted in Figure 1b, assuming that both backbone and grafts obey Gaussian statistics. Because the largest contributions to α_ϵ arise from chemical potential fluctuations with values of k^{-1} that are smaller than either the linear polymer radius of gyration R_1 or the branched polymer *backbone* radius of gyration $R_{LQ} = b(LQ/6)^{1/2}$, the expressions for the $S_i(k)$ can be simplified for this restricted range of k. For such k, we find, for the linear polymer,

$$S_1(k) \approx \frac{2}{(k\beta)^2} \tag{3.19}$$

where $\beta^2 = b^2/(6v)$, while for the branched species,

$$S_2(k) \approx \frac{v}{L + M}\Bigg\{L^2 g(x_L) + M^2 g(x_M) + 2LMh(x_L)\,h(x_M) + 2L^2 x_L^{-1} h(x_L) + 2LMx_L^{-1} h(x_M)[1 + \exp(-x_L)] + 2M^2 h^2(x_M)\frac{\exp(-x_L)}{1 - \exp(-x_L)}\Bigg\} \tag{3.20}$$

In this expression, we have again used the notation $x_i = (kR_i)^2$, with radii of gyration $R_L^2 = Lb^2/6$ and $R_M^2 = Mb^2/6$.

Substitution of the above expressions into eq 2.12 leads to a rather complicated integral for α_ϵ. Neglecting the contributions from $k < R^{-1}$, where R is a large length scale corresponding to the smaller of R_1 and R_{LQ}, and rescaling the integral according to $x = kR_M$, α_ϵ can be written

$$\alpha_\epsilon = \frac{w(\phi, L/M)}{\pi^2 R_M^{\,3}} \tag{3.21}$$

Table 1. Values of $w(\phi, L/M)$

	L/*M*						
ϕ	0.1	0.2	0.5	1.0	2.0	5.0	10.0
0	0.2171	0.1274	0.05870	0.02933	0.01275	0.003304	0.001017
0.1	0.2395	0.1379	0.06173	0.03028	0.01300	0.003337	0.001022
0.2	0.2671	0.1505	0.06520	0.03133	0.01327	0.003370	0.001028
0.3	0.3020	0.1659	0.06920	0.03247	0.01355	0.003404	0.001034
0.4	0.3473	0.1851	0.07386	0.03374	0.01385	0.003440	0.001040
0.5	0.4085	0.2098	0.07938	0.03515	0.01417	0.003476	0.001046
0.6	0.4950	0.2427	0.08603	0.03673	0.01451	0.003513	0.001052
0.7	0.6261	0.2885	0.09419	0.03852	0.01487	0.003552	0.001058
0.8	0.8462	0.3565	0.10446	0.04055	0.01526	0.003591	0.001064
0.9	1.2856	0.4677	0.11782	0.04290	0.01568	0.003632	0.001071
1.0	2.5580	0.6821	0.13596	0.04563	0.01613	0.003674	0.001077

where $w(\phi,\lambda)$ is the following dimensionless function of blend composition ϕ and the ratio of graft spacing to length, $\lambda = L/M$:

$$w(\phi,\lambda) = \frac{1}{8}\int_0^\infty \mathrm{d}x\, x^2\left[\frac{2(1+\lambda) - S(x^2,\lambda)}{2(1+\lambda)\phi + (1-\phi)S(x^2,\lambda)}\right]^2 \tag{3.22}$$

The function $S(y,\lambda)$ appearing in the integrand of the above expression is defined by

$$S(y,\lambda) = \lambda^2 y g(\lambda y) + y g(y) + 2\lambda y h(y)\,h(\lambda y) + 2\lambda h(\lambda y) + 2h(y)[1 + \exp(-\lambda y)] + 2yh^2(y)\frac{\exp(-\lambda y)}{1 - \exp(-\lambda y)} \tag{3.23}$$

In Table 1 we have collected values of the function $w(\phi, L/M)$ for a range of compositions and values of the architectural ratio L/M. In all cases we see that α_ϵ scales as R_M^{-3}, is positive, and increases monotonically with increasing ϕ. This composition dependence is most pronounced for small values of the ratio L/M, i.e., cases of frequent long branches. Thus, as in the previous section, we obtain the prediction that it is thermodynamically less favorable to mix a small amount of a branched component with a linear melt than to mix a small amount of linear component with a branched melt.

The spinodal equation for the linear/branched blend can be written in dimensionless form as

$$\frac{1}{\phi} + \frac{1}{(V_2/V_1)(1-\phi)} - 2\alpha_\epsilon V_1 = 0 \tag{3.24}$$

If the two components have roughly the same overall molecular volumes, i.e., $V_1 \approx V_2$, then the homogeneous mixed phase will lose stability for values of α_ϵ that are of order V_1^{-1}. Based on the above estimates of α_ϵ, this will occur when $R_M^3 \sim V_1$, or when the graft length M (assumed to be of the same order of magnitude as the mean spacing between grafts, L) is of order $N_1^{2/3}$. For grafts that are shorter and more closely spaced than this critical value, the present analysis based on the Gaussian approximation predicts phase separation of the linear and branched components. In the more general case of $L \neq M$, as treated explicitly in Table 1, it is possible to show that an approximate criterion for phase separation is

$$\sigma \equiv \frac{1}{L + M} \sim \frac{b^2}{V_S^{\,2/3}} \tag{3.25}$$

where σ is the fraction of branch points on species 2 and V_S is defined as the minimum of V_1 and V_2.

It is important to emphasize that phase separation of branched/linear mixtures of chemically identical polymers, according to the above criterion, should be easy to realize in practice. Indeed, an extreme example (for which the

Gaussian assumption is inapplicable) would be a blend of linear polyethylene (PE) with poly(ethylethylene) (PEE). PEE can be thought of as a branched polymer of the type shown in Figure 1b, with $L \approx M \approx 1$. The fraction of branch points σ is thus of order unity for PEE and greatly exceeds the quantity on the right-hand side of eq 3.25 for even modest molecular weights. Thus, PE and PEE would not be expected to mix, and this proves experimentally to be the case. Of course, the proper approach to modeling this specific blend, where the branches are not sufficiently long and dilute for Gaussian chain statistics to apply, is to describe both components as *linear homopolymers* with different values of β, following the procedure outlined in section III.A. Indeed, based on experimental measurements of pure component statistics, the asymmetry parameter $\epsilon = (\beta_{\mathrm{PE}}/\beta_{\mathrm{PEE}})^2$ turns out to be $\sim$3.1 for this binary blend. By applying eq 3.3, this is again consistent with the observed immiscibility of the PE–PEE blend.

A more practical example of this class of mixtures is the controversial case of linear and branched polyethylenes (i.e., high and low density). Recent experiments by Hill, Barham, and co-workers[26,27] have led to the authors to conclude that mixtures of these compounds will phase separate under certain conditions of temperature, composition, molecular weight, and branch content. However, their results have been questioned by Alamo et al.,[28] who find complete miscibility under all melt conditions for similar blends. A comprehensive discussion of these results is beyond the scope of our presentation. Furthermore, certain experimental complications, most notably the influence of isotope effects on some of the measurements, should be evaluated before a quantitative assessment is undertaken. It should also be noted that the branched polyethylenes do not conform to the model architecture depicted in Figure 1b; a treelike structure is probably more appropriate. Nevertheless, we can comment on certain of the trends reported.

Overall, the findings of Alamo et al.[28] are much more consistent with our theoretical predictions than the phase separation behavior reported by Hill, Barham, and coworkers.[26,27] In particular, the reported two-phase region above the crystallization temperature occurs for mixtures rather highly enriched in the branched component, opposite to what we anticipate on the basis of the above model calculations. Moreover, the finding[26] that this two-phase region shrinks in size as the branch content is increased is not in accord with the present theory. Obviously, more experimental and theoretical attention should be paid to this important class of architecturally asymmetric mixtures.

IV. Discussion and Conclusions

In the present paper we have demonstrated how a relatively simple field-theoretic approach can be used to identify universal and quasi-universal features of the thermodynamics of nearly athermal polymer blends. Specifically, we have uncovered entropic corrections to the Flory–Huggins theory that reflect differences in conformational and packing properties of the pure components and differences in gross architectural features such as degree of branching. The universal nature of these corrections results from the fact that they are associated with intra- and intermolecular correlations of species density on length scales intermediate between the statistical segment size and the radius of gyration scale. In principle, corrections such as these that are independent of local chemical details, but sensitive to mesoscale conformational and architectural properties, are contained in more microscopic approaches such as those based on classical liquid state theory.[8–11,17] However, their universal character is frequently masked by the inclusion of complex *local* liquid structure in such approaches. The present work provides an explicit demonstration of the power of coarse-grained field-theoretic methods for elucidating corresponding-states-like principles in polymer–polymer thermodynamics.

Our model of polymer blends, while highly simplified, should prove useful for decribing certain classes of nearly athermal mixtures, most notably polyolefins. By assuming an athermal reference state and enforcing incompressibility, we implicitly restrict consideration to blends in which the entropic contributions to the excess free energy associated with *nonlocal* conformational or architectural differences between components dominate heat of mixing contributions or *purely local* entropic effects. For a number of binary polyolefin mixtures containing PE, PEE, PEP, poly(vinylcyclohexane), and various copolymers constructed from these components, we have demonstrated[14,29] that a strong correlation exists between the observed phase behavior and the predictions of the present work. In other blends for which enthalpic effects are likely more important, the effective interaction parameter α will generally have significant entropic and enthalpic components. Although there is no reason to believe that these effects are purely additive,[17,30] a rough method of assessing their relative importance in a particular blend would be to estimate the nonlocal entropic contributions, i.e., α_ϵ, by means of the present theory and then compare the result with an estimation of α by traditional (enthalpic) methods based on solubility parameters.

A very important outcome of the present work is a set of molecular design criteria for developing new miscible polymer blends. Based on the above discussion, we anticipate that these criteria will prove most useful for polyolefin mixtures, where heats of mixing are small and specific, highly directional local interactions are absent. In particular, we have established the appropriate mixing rules for designing a linear copolymer component, either block or random, that will prove miscible with a desired polyolefin homopolymer. Implementation of this strategy simply requires measurements (or empirical estimates) of *pure component* radii of gyration, densities, molecular weights, and copolymer compositions. Fortunately, the experimental data required to calculate the pure component conformational parameter β, which plays a prominant role in our design strategy, are available in the literature[14,15,22,29] for a substantial number of important polyolefins. Thus, it is possible without additional experiments to identify several homopolymer/copolymer pairs as candidates for partial or complete miscibility. Indeed, successful implementation of the above scheme to match the effective β's of the two components has been demonstrated in one of our laboratories[14] for a mixture of PEP homopolymer with a PE–PEE random copolymer. Further experiments on other model homopolymer/random copolymer and homopolymer/block copolymer mixtures would prove extremely valuable in testing our design strategy.

The theory presented in the above sections is in an early stage of development, yet has already yielded valuable insights into polyolefin phase behavior. Future studies will be concerned with establishing the accuracy and validity of the Gaussian approximation for the functional integral employed here. Moreover, it is desirable to relax the assumptions of incompressibility and vanishing enthalpic contributions to α. The assumption of Gaussian statistics in parameterizing the single-chain structure factors $S_i(k)$, while simplifying, is not crucial to the application of the theory. In particular, if the $S_i(k)$ are known from experimental scattering measurements on the pure components, eq 2.10 or 2.12 can be numerically evaluated to analyze phase behavior. Such a procedure may prove to be particularly important for highly branched systems, where deviations from Gaussian statistics can be significant. We also plan to investigate extensions of the theory to other architectures and to include effects associated with polydispersity, random branching, and chemical disorder. Particularly obvious and important extensions are to consider mixtures of two or more copolymers and mixtures containing branched molecules designed to mimick the low-density polyethylene architecture. Furthermore, we intend to use the present approach to treat conformational asymmetry effects on the order–disorder transition of block copolymer melts.

From an experimental standpoint, a high priority is to confirm the predicted trends with varying conformational asymmetry (ϵ) and blend composition for a large number of well-characterized polyolefin blends. Recent experiments by Gehlsen and Bates[29] on a series of three symmetric, unsaturated (diene) diblock copolymers and their fully hydrogenated counterparts conclusively demonstrate that the location of the order–disorder transition in block copolymers can be rationalized in terms of arguments similar to those used in section III.A based on the value of ϵ. Much less data is available on the thermodynamic properties of well-characterized linear/branched mixtures, such as those treated in sections III.C and III.D. Scattering measurements on blends of chemically identical, but partially deuterated, linear and star molecules would be invaluable in testing our predictions for the dependence of α_ϵ on the arm number, arm molecular weight, and blend composition.

Acknowledgment. This work was supported by the National Science Foundation under PYI Grants NSF-DMR 9057147 (G.H.F.) and NSF-DMR 8957386 (F.S.B.) and by the Materials Research Laboratory at the University of California, Santa Barbara, under Grant No. DMR 9123048 (A.J.L.). The authors are grateful to David Morse for insightful discussions.

References and Notes

(1) Flory, P. J. *J. Chem. Phys.* **1942**, *10*, 51.
(2) Huggins, M. *J. Phys. Chem.* **1942**, *46*, 151.
(3) Helfand, E.; Sapse, A. M. *J. Chem. Phys.* **1975**, *62*, 1327.
(4) Roe, R. J.; Zin. W. C. *Macromolecules* **1980**, *13*, 1221.
(5) Flory, P. J. *Discuss. Faraday Soc.* **1970**, *49*, 7.
(6) Sanchez, I. C.; Lacombe, R. H. *J. Phys. Chem.* **1976**, *80*, 2352.
(7) Dudowicz, J.; Freed, K. F. *Macromolecules* **1991**, *24*, 5076, 5096.
(8) Hansen, J.-P.; McDonald, I. R. *Theory of Simple Liquids*; Academic: new York, 1986.
(9) Schweizer, K. S.; Curro, J. G. *J. Chem. Phys.* **1990**, *60*, 809.
(10) Curro, J. G.; Schweizer, K. S. *Macromolecules* **1990**, *23*, 1402.
(11) Chandler, D. In *The Liquid State of Matter: Fluids, Simple and Complex*; Montroll, E. W., Leibowitz, J. L., Eds.; North-Holland: New York, 1982; p 275.
(12) De Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(13) Bates, F. S.; Fredrickson, G. H. *Macromolecules* **1994**, *27*, 1065.
(14) Bates, F. S.; Schulz, M. F.; Rosedale, J. H.; Almdal, K. *Macromolecules* **1992**, *25*, 5547.
(15) Krishnamoorti, R.; Graessley, W. W.; Balsara, N. P.; Lohse, D. J., preprint.
(16) Olmsted, P. D.; Milner, S. T., preprint.
(17) Schweizer, K. S. *Macromolecules* **1993**, *26*, 6033, 6050.
(18) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(19) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford: New York, 1986.
(20) Morse, D.; Liu, A. J.; Fredrickson, G. H., unpublished.
(21) For example, the system poly(ethylenepropylene) (PEP) and poly(ethylethylene) (PEE), for which $\epsilon = (\beta_{\mathrm{PEP}}/\beta_{\mathrm{PEE}})^2 \approx 2.1$, has an asymmetric phase diagram with a significantly larger single-phase window on the PEE-rich side. Bates, F. S., et al., unpublished results.
(22) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zierkel, A., preprint.
(23) Benoit, H.; Hadziioannou, G. *Macromolecules* **1988**, *21*, 1449.
(24) Faust, A. B.; Sremcieh, P. S.; Gilmer, J. W.; Mays, J. W. *Macromolecules* **1989**, *22*, 1250.
(25) Russell, T. P.; Fetters, L. J.; Clark, J. C.; Bauer, B. J.; Han, C. C. *Macromolecules* **1990**, *23*, 654.
(26) Hill, M. J.; Barham, P. J.; van Ruiten, J. *Polymer* **1993**, *34*, 2975. Barham, P. J.; Hill, M. J.; Goldbeck-Wood, G.; van Ruiten, J. *Polymer* **1993**, *34*, 2975.
(27) Oiarzabal, L.; Higgins, J. S.; Hill, M. J.; Barham, P. J. *Polymer*, submitted.
(28) Alamo, R. A.; Londono, J. D.; Mandelkern, L.; Stehling, F. C.; Wignall, G. D. *Macromolecules*, to appear.
(29) Gehlsen, M. D.; Bates, F. S. *J. Polym. Sci., Polym. Phys. Ed.*, submitted.
(30) Olvera de la Cruz, M.; Sanchez, I. C.; Edwards, S. F. *J. Chem. Phys.* **1988**, *89*, 1704.