Theory for the Phase Behavior of Polyolefin Blends: Application to the Polyethylene/Isotactic Polypropylene Blend

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ABSTRACT: A microscopically realistic theory for modeling the structure, thermodynamics, and phase behavior of polyolefin blends is developed on the basis of the polymer reference interaction site model (PRISM theory). The thermodynamics of mixing is treated using perturbation theory with the corresponding athermal mixture as the reference system. As an illustration of the approach we modeled the polyethylene/isotactic polypropylene blend (PE/i-PP). The polypropylene monomers were constructed from three independent interaction sites representing the CH_2, CH, and CH_3 united atom groups constituting the monomer. Likewise polyethylene monomers consisted of two identical interaction sites, each representing a CH_2 moiety. The intramolecular structure functions, required as input to PRISM theory, were determined from single-chain Monte Carlo simulations using the rotational isomeric state approximation. The Suter–Flory rotational isomeric state parameters were used for isotactic polypropylene. PRISM theory was used to compute the ten independent intermolecular pair correlation functions needed to characterize the intermolecular packing of the athermal blend. The enthalpic contribution to the free energy was then computed from first-order perturbation theory. The entropy of mixing, heat of mixing, and spinodal curve were computed as a function of composition for the blend consisting of PE and i-PP chains of 200 monomer units. The blend was found to be highly incompatible with UCST behavior. Local or short range correlations were found to significantly increase the heat of mixing, resulting in critical temperatures approximately 10–15 times larger than predicted on the basis of Flory–Huggins theory under the assumption of random mixing.

I. Introduction

Blends of polyolefin chain molecules represent a class of technologically important materials[1] whose properties have been studied at or near room temperature by many investigators.[2,3] Since polyolefin polymers are frequently crystalline at room temperature, blends of these components usually phase separate and exhibit complex morphology in the solid state due to crystallinity effects. An important question which arises is, do polyolefin blends phase separate in the liquid phase above the melting temperatures of the components? This question has been studied recently for a range of branched polyolefin blend systems by several groups.[4-8] Based on neutron and light scattering measurements, a rich dependence of the phase behavior is observed as a function of the architecture of the polyolefin chain molecules. UCST behavior is generally observed,[4] and interesting unsymmetrical deuterium substitution effects have been reported.[5,6] The purpose of this investigation is to develop a theory for the phase behavior of polyolefin blends. This will be accomplished in the context of the polyethylene/isotactic polypropylene blend (PE/i-PP), but the methods outlined in this paper would apply more generally to blends of vinyl polymers.

Although the authors are not aware of any systematic studies of the phase behavior of the PE/i-PP blend in the melt, it is generally accepted that they are strongly

incompatible. Wignall and co-workers[3] studied a deuterated PE/i-PP sample quenched from the melt at 200 °C with SANS and concluded that phase separation existed in the melt. Lohse[8] employed SANS to study blends of i-PP with ethylene/propylene random copolymers of varying compositions. Phase separation was observed in the melt for copolymer compositions above 8% ethylene. Because one would expect that the interactions between the various repeat units in the polyolefin blend to be similar, on the basis of Flory–Huggins theory,[9] it is surprising that the PE/i-PP blend is apparently so highly incompatible. In this study we will model the phase behavior of the PE/i-PP blend in a realistic fashion using the polymer reference interaction site model[10] (PRISM theory).

A possible explanation of the diverse dependence of miscibility on chemical architecture in polyolefins is related to the packing of the chains in the liquid mixture. Previous PRISM calculations on athermal mixtures[10-11] of various freely-jointed chains demonstrated that local structural asymmetry in the monomer structure leads to significant, nonuniversal deviations from random packing. No phase separation was observed in these athermal blend calculations. Interestingly, these calculations indicated that the RPA χ parameter, defined for a hypothetical incompressible blend, actually decreases with increasing structural asymmetry. Although it was not appreciated at the time,[11] this does not imply that the athermal mixture becomes more stable with increasing asymmetry, but rather reflects the importance of compressibility effects[10] in blend miscibility.

Bates and co-workers[7,12,13] have pointed out that asymmetry in the statistical segment lengths of the respective components can lead to *packing frustration* and an unfavorable entropy of mixing in the purely athermal blend. Fredrickson, Liu, and Bates[13] have estimated this contribution on the basis of a coarse-grained, field theoretic calculation for an athermal blend of Gaussian chains. Their results indicate that immiscibility in polyolefin blends is attributable solely to phase separation in the purely athermal mixture. In the current investigation we will argue that the heat of mixing, controlled by local correlations, also plays an important, if not crucial, role in polyolefin blend miscibility.

A unique and powerful feature of PRISM theory is its ability to account for intermolecular packing on both the local (monomeric) and global (correlation hole) length scales. Since the van der Waals interactions between the atomic species making up the chains in the mixture are short range, it is our feeling that the local correlations in packing, caused by chemical architecture, must play an important role in controlling the highly nonuniversal phase behavior in polyolefin blends. Hence in the present investigation we attempt to model the PE/i-PP blend in a molecularly realistic fashion. In our PRISM treatment, isotactic polypropylene chains are modeled by N monomers each containing three independent sites A, B, and C, representing the CH_2, CH, and CH_3 moieties, respectively. Polyethylene is considered to consist of N monomers of two identical D sites, each representing a CH_2 group along the chain backbone. The necessary intramolecular information is input to PRISM theory on the basis of Flory's rotational isomeric state calculations for polyethylene[15] and the Suter–Flory rotational isomeric state model for isotactic polypropylene.[16] The thermodynamics of the PE/i-PP blend will be treated using perturbation theory in which the purely athermal blend plays the role of the reference system.

An intermediate approach, using PRISM theory on a model in which each monomer is coarse grained into spherical sites, has been carried out by Schweizer and collaborators.[14] In this intermediately coarse grained model the chain stiffness is adjusted to match experimental data on the pure component melts. Some trends could then be predicted for the corresponding binary mixtures which are in accord with experiments on branched polyolefins. Honeycutt[14] used a similar coarse-grained model to study PVC/PMMA blends. In the present work we use a multiple site model to construct each monomer in order to more faithfully represent the nonspherical geometry of the vinyl monomer. Furthermore we attempt to include chemically specific effects like rotational potentials and correlations through a rotational isomeric state representation of the single chain structure.

The remainder of the paper is organized as follows: Section II contains a description of the intramolecular and intermolecular structure of the reference athermal system. In section III the thermodynamics are treated using perturbation theory. Finally, the numerical results are presented and discussed in section IV.

II. Athermal System

In this investigation we define an athermal blend to be one in which the heat of mixing is rigorously zero. Hence the free energy of mixing is entirely due to entropy of mixing effects induced by structural asym-
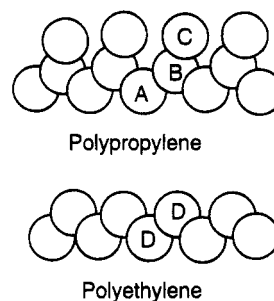
Figure 1. Schematic representation of the multiple site construction of isotactic polypropylene and polyethylene monomers. Bond lengths (angles) are maintained at 1.54 Å (109.5°). Three independent sites A, B, and C are used to represent the CH_2, CH_3, and CH moieties in isotactic polypropylene. One independent site D is used to represent the CH_2 group in polyethylene. The C sites are constrained to the isotactic stereochemical configuration.

metries in the components. These structural asymmetries arise because of the difference in monomer structure and chain architecture between the components. This athermal system will then provide a reference system for the thermodynamics of the real (or thermal) blend in which the enthalpic terms are included via perturbation theory. In this section we will treat the properties of this reference system.

A. PRISM Theory. In order to calculate the intermolecular packing in the polymer mixture we make use of polymer RISM or PRISM theory. PRISM theory was developed by Curro and Schweizer[10,17-24] to describe the intermolecular structure, thermodynamics, and phase behavior of polymer melts and blends. It is an extension to polymers of the successful reference interaction site model (RISM theory) for molecular liquids developed by Chandler and Andersen.[25,26]

Curro[21] applied PRISM theory to freely-jointed vinyl polymer melts in which the monomer structure was modeled by three independent sites leading to six independent pair correlation functions. Yethiraj and co-workers[27] performed Monte Carlo simulations on freely-jointed vinyl chain melts and found good agreement between the six intersite radial distribution functions obtained from the simulation and PRISM theory. More recently, molecular dynamics simulations on freely-jointed, athermal blends were carried out by Stevenson and co-workers.[28] In their investigation excellent agreement was found between the intermolecular radial distribution functions from the MD simulation and from PRISM theory. Such comparisons between PRISM theory and simulation suggest that a multisite treatment of a blend of vinyl polymers would be an accurate description of the athermal mixture. Since PRISM theory has been discussed in detail elsewhere,[17-24] we will only briefly outline its application here.

Consider a system consisting of M_{PP} and M_{PE} polymer molecules of i-PP and PE, respectively. Each monomer is made up of one or more independent interaction sites. In the vinyl polymer i-PP, there are three independent sites: the interaction sites A and B corresponding to the united atom representations of the backbone groups CH_2 and CH, respectively, and the side chain CH_3 group labeled as site C. In Figure 1 we depict the arrangement of sites along the polypropylene chain backbone. The linear molecule PE has no side chain group, and each monomer has only two identical united atom CH_2 groups, each of which can be represented by an independent interaction site D; this is also shown in Figure 1. Thus a blend of i-PP and PE can be represented in

general by four independent interaction sites. The total number of sites in i-PP and PE molecules are $3N_{PP}$ and $N_D = 2N_{PE}$, respectively, where N_{PP} and N_{PE} are the number of monomers in an i-PP and a PE chain. The intermolecular packing in the blend can be conveniently characterized by ten independent, intermolecular radial distribution functions $g_{\alpha\gamma}(r)$ defined between pairs of sites of type A, B, C, or D according to

$$\varrho_\alpha \varrho_\gamma g_{\alpha\gamma}(r) = \left\langle \sum_{i \neq j} \delta(\vec{r}_i^\alpha)\, \delta(\vec{r} - \vec{r}_j^\gamma) \right\rangle \qquad (1)$$

where ϱ_α is the site density of type α and $\vec{r}_i^\alpha$ is the position vector of site α on chain i.

We begin by defining an Ornstein–Zernike type[10,26] (or PRISM) equation relating the radial distribution functions to the direct correlation functions. A generalization of the single site PRISM equation for four sites is straightforward,[21] and it reads in momentum space as

$$\hat{H}_{\alpha\beta}(k) = \sum_{\sigma\lambda} \hat{\Omega}_{\alpha\sigma}(k)\, \hat{C}_{\sigma\lambda}(k)[\hat{\Omega}_{\lambda\beta}(k) + \hat{H}_{\lambda\beta}(k)] \qquad (2)$$

where the circumflex accent denotes Fourier transformation with wave vector k and the Greek indices run over the four sites A, B, C, and D. The functions $H_{\alpha\beta}(r)$ and $\Omega_{\alpha\beta}(r)$ are the elements of 4×4 matrices defined as follows

$$H_{\alpha\beta}(r) = \varrho_\alpha \varrho_\beta h_{\alpha\beta}(r) \qquad (3)$$

$$\Omega_{\alpha\beta}(r) = \tilde{\varrho}_\alpha \sum_{i\in\alpha, j\in\beta} \omega_{ij}(r) \qquad (4)$$

with $\tilde{\varrho}_\alpha$ defined as the chain density ($\tilde{\varrho}_\alpha = \varrho_\alpha/N_\alpha$) where N_α is the number of sites of type α per chain. $\omega_{ij}(r)$ is the normalized probability density between i and j sites, and $h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1$ is the total correlation function between the α and β type sites.

The $C_{\alpha\gamma}(r)$ elements are referred to as the direct correlation functions and are defined through the set of PRISM equations in eq 1. To determine the intermolecular pair correlation functions another set of relations or "closure" conditions between $h_{\alpha\beta}(r)$ and $C_{\alpha\beta}(r)$ are required. Following Chandler and Andersen,[10,25,26] we propose that the direct correlation functions be approximated by the Percus–Yevick theory (PY) of atomic liquids.[29] For hard-core potentials the PY closure has the following simple form

$$g_{\alpha\beta}(r) = 0 \quad \text{for} \quad r < d_{\alpha\beta} \qquad (5a)$$

$$C_{\alpha\beta}(r) \cong 0 \quad \text{for} \quad r > d_{\alpha\beta} \qquad (5b)$$

where $d_{\alpha\beta}$ are effective hard-core distances between the α and β type of sites. In previous studies[10] on the PRISM theory of blends it was discovered that use of the PY and MSA closures to account for attractive interactions leads to incorrect scaling of the spinodally-derived critical temperature with molecular weight. (Chandler[26] has pointed out that the critical temperature obtained from the free energy has the correct scaling.) We feel that this thermodynamic consistency problem can be avoided through using perturbation theory with the athermal blend as a reference system. On the basis of the recent molecular dynamics simulations of Stevenson[28] discussed earlier, we feel that the

PY closure is justified here to describe athermal blends where only repulsive interactions are in effect.

For given chemical architectures of the chains specified through the $\Omega_{\alpha\gamma}(r)$ functions, eqs 2 and 5 constitute the multiple site PRISM theory for the athermal blend of PE and PP. In this case ten coupled integral equations result which can be solved numerically with Picard iteration techniques. The Picard iteration scheme used here is a generalization of the methods used previously to describe vinyl chain melts.[21]

B. Intramolecular Architecture. The chemical architecture, which distinguishes one polymer from another, enters the PRISM theory solely through the intramolecular structure functions $\hat{\Omega}_{\alpha\gamma}(k)$ defined in eq 4. Since the chains are flexible and can undergo internal rotations, one might surmise that the intramolecular structure functions $\hat{\Omega}_{\alpha\gamma}(k)$ have to be calculated self-consistently with the intermolecular pair correlation functions $g_{\alpha\gamma}(r)$. Such self-consistent calculations are possible and have been carried out previously on melts.[30–32] At melt densities, however, intramolecular excluded volume effects are screened and to a very good approximation[10] we can avoid the self-consistency calculations by making use of Flory's ideality hypothesis. Further justification for the ideality assumption in melts is supported by SANS experiments[33] on melts and computer simulations on blends.[28] Thus we can considerably simplify the problem by calculating the intramolecular structure functions $\hat{\Omega}_{\alpha\gamma}(k)$ from two separate single chain calculations on polyethylene and isotactic polypropylene in which long range repulsive interactions are intentionally set to zero.

In this investigation we model the intramolecular structure of PE and i-PP in a realistic fashion with the rotational isomeric state model.[15] We obtained the required $\hat{\Omega}_{DD}(k)$ function for polyethylene by employing an approach used in previous studies.[34] In this method $\hat{\Omega}_{DD}(k)$ is divided into short and long range contributions according to

$$\hat{\Omega}_{DD}(k) = \frac{1}{N}\sum_\alpha \left[\sum_{|\alpha-\beta|\leq 5} \hat{\omega}_{\alpha\beta}(k) + \sum_{|\alpha-\beta|>5} \hat{\omega}_{\alpha\beta}(k) \right] \qquad (6)$$

The first term for $|\alpha - \gamma| \leq 5$ is determined by exact enumeration of the rotational isomeric states for the PE chain backbone. The long range term, for which $|\alpha - \gamma| > 5$, is estimated[10,34] from the "Koyama distribution" of a semiflexible chain where the second $\langle r_{\alpha\beta}^2 \rangle$ and fourth moments $\langle r_{\alpha\beta}^4 \rangle$ are chosen to match the complete rotational isomeric state model.[15] This procedure for calculating $\hat{\Omega}_{DD}(k)$ for polyethylene was found to be in excellent agreement with the complete Monte Carlo simulation for a rotational isomeric state chain.[34] The results are shown in Figure 2a for polyethylene at 473 K.

The situation regarding the appropriate rotational isomeric state model for i-PP is not as clear as with PE. As pointed out by Zirkel and co-workers[35] there are at least eight different rotational isomeric state parameterizations of i-PP. The characteristic ratio C_∞ of a polymer chain is given as $C_\infty = \langle r^2 \rangle/l^2N$, where $\langle r^2 \rangle$ is the average end to end distance, l is the bond length, and N is the total number of backbone sites. Unfortunately, the characteristic ratio and its temperature coefficient vary considerably depending on whose parameters are used. In the present study we chose, somewhat arbitrarily, to use the rotational isomeric state model of Suter and Flory[16] for i-PP. For this model
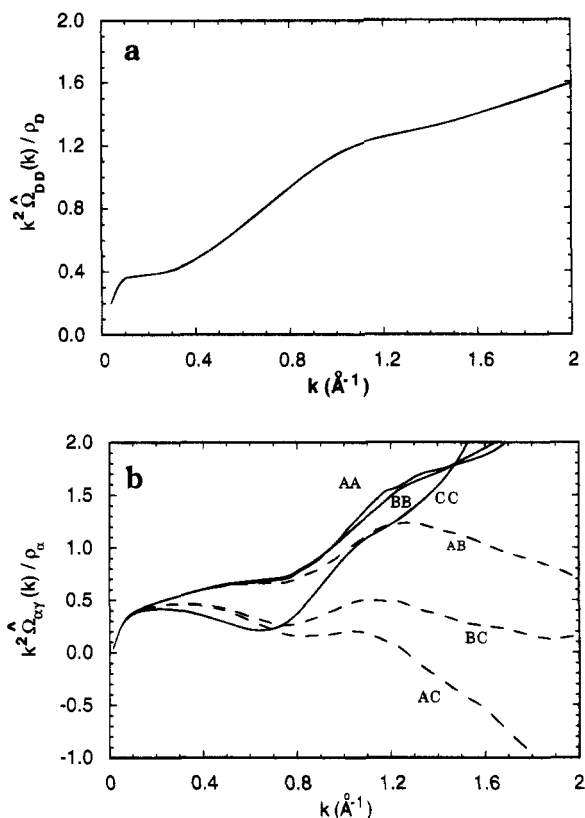
Figure 2. (a) Kratky plot of the intramolecular (single chain) structure factor for polyethylene of 200 monomers (400 repeat units). The calculation was made using the rotational isomeric state model of Flory.[15] (b) Kratky plot of the intramolecular (single chain) structure factors for isotactic polypropylene of 200 monomer units. The calculation was made using the rotational isomeric state model of Suter and Flory[16] where the energies are rescaled to obtain a characteristic ratio of 6.2.

the characteristic ratio at 473 K indicates the chain is collapsed relative to polyethylene with $C_\infty = 6.7$. On the basis of SANS measurements by Ballard and co-workers,[36] the experimental characteristic ratio for i-PP in the melt is approximately $C_\infty = 6.2$ and appears to be roughly independent of temperature. In order to compensate for the discrepancy between Suter–Flory i-PP and experiment, we adjusted the temperature until a characteristic ratio of 6.2 (at $T = 286$ K) was obtained. Such a procedure is equivalent to rescaling the rotational energies in the Suter–Flory model. The six intramolecular structure functions $\hat{\Omega}_{\alpha\gamma}(k)$ found for i-PP by this procedure are depicted in Figure 2b. In the intermediate scaling regime these structure functions are qualitatively similar to the freely jointed chain structure functions obtained recently by Curro[21] for vinyl chains. At higher wave vectors k the $\hat{\Omega}_{\alpha\gamma}(k)$ functions show details which are highly specific to the i-PP molecule.

Strictly speaking, the intramolecular structure factors for both PE and i-PP are temperature dependent. Because the experimental characteristic ratio of i-PP appears to be independent of temperature, and the temperature dependence of PE is fairly weak,[15] we will neglect the temperature dependence of the intramolecular structure in the present study. The structure functions for PE at 473 K and i-PP at 286 K, shown in Figure 2, will be used to calculate the intermolecular packing in the athermal mixture.

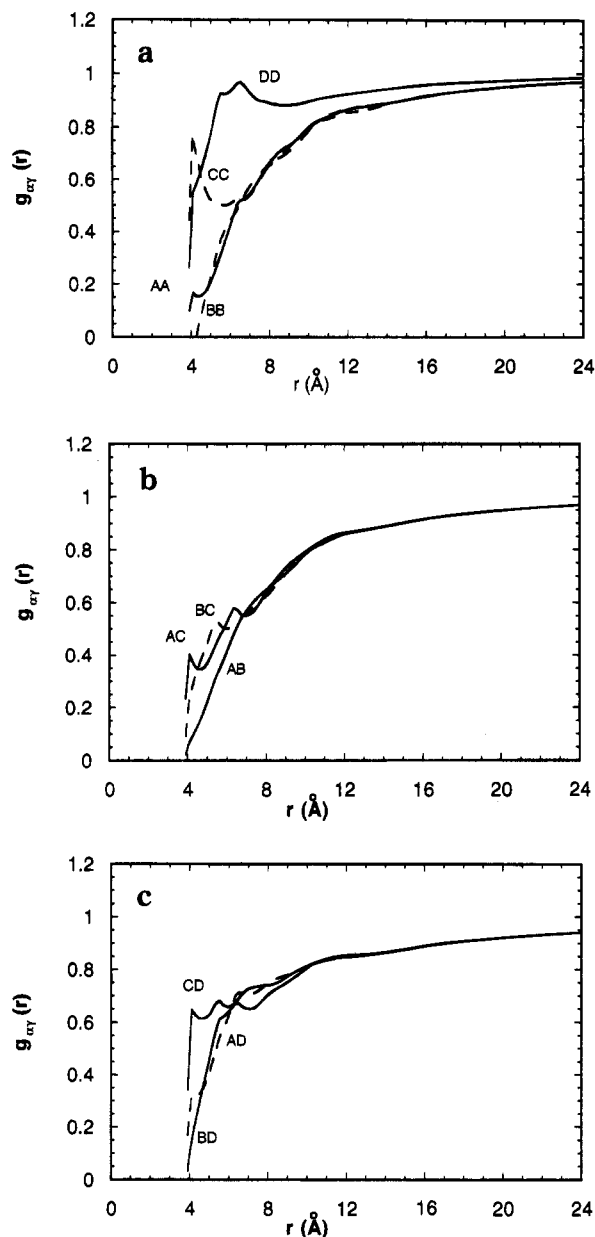**C. Intermolecular Packing.** In our present analysis of the PE and i-PP blend, we studied the inter-

molecular structure of i-PP consisting of 200 monomer units (400 backbone sites) and PE of 400 backbone sites at a meltlike packing fraction for the mixture. The effective hard sphere diameter of the CH_2 group in polyethylene is taken to be 3.9 Å; this choice has been found to match very well with wide angle X-ray measurements on PE melts.[37,38] Furthermore, recent studies[39] suggest that the CH and CH_3 groups in alkanes have effective hard sphere diameters similar to that of the methylene group. Hence in this investigation we will take the effective hard core of all three sites in the i-PP monomer also to be 3.9 Å. These hard-core sites are overlapping sites since the bond length is maintained at 1.54 Å and the bond angles along the i-PP (PE) backbone are held fixed at 109.5° (112°), respectively.

The PRISM theory was employed with the intramolecular structure factors shown in Figure 2 for PE and i-PP to calculate the intermolecular packing. The ten independent radial distribution functions $g_{\alpha\gamma}(r)$ were obtained by numerical solution of the ten integral equations given by eqs 2 and 5 using a Picard iteration scheme.[21] The algorithm begins by assuming $\Gamma(r) = H(r) - C(r)$ at 2048 equally spaced points in r space. The closure condition in eqs 5 is then used to compute the $C(r)$ from $\Gamma(r)$, which is then fast Fourier transformed to give $\hat{C}(k)$ at 2048 equally spaced intervals in k space. The 4×4 matrix equations in eq 2 are then solved numerically to give a new estimate of $\hat{\Gamma}(k)$ in k space. After carrying out another fast Fourier transform back to r space, the new $\Gamma(r)$ is compared with the previous estimate. A solution is assumed when the average fractional difference between estimates is less than some tolerance (usually 10^{-7}). If convergence is not obtained, the above procedure is repeated using a new guess for $\Gamma(r)$.

The ten intermolecular radial distribution functions $g_{\alpha\gamma}(r)$'s calculated from PRISM for an athermal blend of PE and i-PP at $\phi = 0.5$ are shown Figure 3. It can be seen from these figures that all the various $g_{\alpha\gamma}(r)$'s approach each other in a universal manner on a long range, R_g length scale for which $g(r)$ approaches 1 from below. This is the correlation hole[42] regime and is a consequence[10] of the screening of a pair of intermolecular sites on two chains by the remaining intramolecular sites on these same two chains.

On short length scales it can be seen in Figure 3 that the $g_{\alpha\gamma}(r)$'s exhibit detailed, nonuniversal structure. These local intermolecular packing effects are a result of the detailed intramolecular architecture of the polymer chains entering the PRISM theory through $\hat{\Omega}_{\alpha\gamma}(k)$. One would expect these local pair correlations to play an important role in determining the heat of mixing of the blend since the van der Waals interactions between sites is short range. Note that all the $g_{\alpha\gamma}(r)$'s are zero inside the 3.9 Å hard core as required by eq 5a. It is interesting to note that $g_{BB}(r)$, between CH groups on different chains, approaches zero at 4.3 Å, even though d_{BB} is set at 3.9 Å. This is a "cage effect" in which the CH backbone groups tend to be shielded by adjacent intramolecular sites, thus preventing intermolecular CH groups from coming in close proximity.
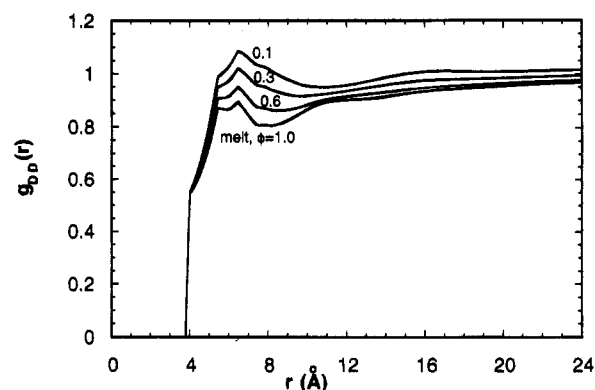
One can also notice in Figure 3 that $g_{CC}(r)$ is larger than $g_{AA}(r)$ and $g_{BB}(r)$ at short distances. This trend is also a shielding effect[21,27] which can be understood intuitively. Because the methyl side groups on i-PP are on the outside of the chain backbone, they are more accessible than backbone A and B sites which are shielded. Hence they can approach each other more
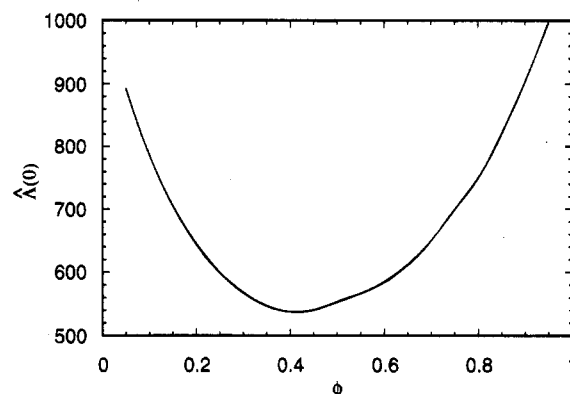
Figure 4. Intermolecular radial distribution function $g_{DD}(r)$ for polyethylene in the blend at various volume fractions ϕ of polyethylene as labeled. Note that $g_{DD}(r)$ increases as ϕ decreases, suggesting that the polyethylene tends to cluster in the blend relative to the melt.

Figure 5. $\hat{\Lambda}(k) = \det(1 - \hat{\Omega}(k)\hat{C}(k))$ at zero water vector as a function of composition for an athermal PE/i-PP blend. Since $\hat{\Lambda}(0) > 0$ over the complete concentration, we infer that spinodal composition does not occur in this athermal system.

of intermolecular contacts of polyethylene chains increases in the blend relative to the melt. One could view this as a tendency for the polyethylene to cluster in the blend due to unfavorable cross correlations between PE and i-PP chains in the blend.

Figure 5 demonstrates that even though there is some microscopic clustering of PE chains, the athermal blend is not macroscopically phase separated. To see this, one can define a 4×4 structure factor matrix according to

$$\hat{S}_{\alpha\gamma}(k) = \hat{\Omega}_{\alpha\gamma}(k) + \hat{H}_{\alpha\gamma}(k) \qquad (7)$$

Equation 2 can be used to eliminate $\hat{H}_{\alpha\gamma}(k)$ in eq 7 in favor of the direct correlation functions which leads to

$$\hat{S}(k) = (1 - \hat{\Omega}(k)\hat{C}(k))^{-1}\cdot\hat{\Omega}(k) \qquad (8)$$

By carrying out the matrix operations in eq 8 it can be seen that the matrix elements $\hat{S}_{\alpha\gamma}(k)$ will diverge when the quantity $\hat{\Lambda}(k) = \det(1 - \hat{\Omega}(k)\hat{C}(k))$ approaches zero. Spinodal decomposition would be expected to occur in a polymer blend when $\hat{\Lambda}(0) = 0$ at zero wave vector k. In Figure 5 we have plotted $\hat{\Lambda}(0)$ as a function of composition for the PP/i-PP athermal blend reference system. Since $\hat{\Lambda}(0)$ remains positive at all compositions, no spinodal decomposition is occurring in our athermal system.

III. Thermodynamics of Mixing

In a real polymer blend (thermal blend) any energy asymmetries in the van der Waals interactions leads

Figure 3. (a) Intermolecular radial distribution functions for the athermal blend PE/i-PP ($N_{PE} = N_{PP} = 200$) obtained from PRISM theory. Each curve corresponds to $g_{\alpha\gamma}(r)$ for a pair of intermolecular sites α and γ as labeled. Diagonal elements of $g_{\alpha\gamma}(r)$. (b) Intermolecular radial distribution functions for the athermal blend PE/i-PP ($N_{PE} = N_{PP} = 200$) obtained from PRISM theory. Each curve corresponds to $g_{\alpha\gamma}(r)$ for a pair of intermolecular sites α and γ as labeled. Polypropylene cross terms. (c) Intermolecular radial distribution functions for the athermal blend PE/i-PP ($N_{PE} = N_{PP} = 200$) obtained from PRISM theory. Each curve corresponds to $g_{\alpha\gamma}(r)$ for a pair of intermolecular sites α and γ as labeled. PE/i-PP cross terms.

readily. In fact the relative ordering of all the various $g_{\alpha\gamma}(r)$ in Figure 3 can be qualitatively understood on local or monomeric length scales from simple shielding arguments.

The intermolecular radial distribution functions will, of course, be composition dependent. In the case of the PP/i-PP blend under study, we observed that the pair correlation function $g_{DD}(r)$ attributable to polyethylene has significantly more composition dependence than the $g_{\alpha\gamma}(r)$ associated with i-PP. This is seen in Figure 4 where $g_{DD}(r)$ is plotted for various compositions. It is interesting to observe that the primary peak near 5.5 Å grows in size as the concentration is decreased from the melt. This suggests qualitatively that the number

to a positive heat of mixing that, in principle, can drive phase separation. In our approach to the thermodynamics of mixing we will assume that the attractive branches of the van der Waals interactions are weak relative to k_BT. This allows us to account for the attractions in a convenient way by employing perturbation theory.[29]

A. Heat of Mixing. For convenience we take the potential energy $v_{\alpha\gamma}(r)$ between two intermolecular sites α and γ to be of the Lennard-Jones form

$$v_{\alpha\gamma}(r) = 4\epsilon_{\alpha\gamma}\left[\left(\frac{\sigma_{\alpha\gamma}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\gamma}}{r}\right)^{6}\right] \quad (9)$$

This pair potential $v_{\alpha\gamma}(r) = u_{\alpha\gamma}(r) + w_{\alpha\gamma}(r)$ can be naturally decomposed into a purely repulsive branch $u_{\alpha\gamma}(r)$ and an attractive branch $w_{\alpha\gamma}(r)$ according to[29]

$$u_{\alpha\gamma}(r) = v_{\alpha\gamma}(r) \quad \text{for } r \le \sigma_{\alpha\gamma}$$
$$= 0 \quad \text{for } r > \sigma_{\alpha\gamma} \quad (10a)$$

$$w_{\alpha\gamma}(r) = 0 \quad \text{for } r \le \sigma_{\alpha\gamma}$$
$$= v_{\alpha\gamma}(r) \quad \text{for } r > \sigma_{\alpha\gamma} \quad (10b)$$

With this decomposition the purely repulsive blend, in which the sites interact via $u_{\alpha\gamma}(r)$ potentials, corresponds to our reference athermal blend studied in the previous section. In this case the athermal blend site diameters $d_{\alpha\gamma}$ are effective hard-core diameters corresponding to the Lennard-Jones soft repulsion.[26,29]

The Helmholtz free energy A can be written[26,29] in the form

$$\frac{\beta A}{V} = \frac{\beta A_o}{V} + \frac{1}{2}\sum_{\alpha\gamma}\varrho_\alpha\varrho_\gamma \int \beta w_{\alpha\gamma}(r)\, g_{\alpha\gamma}(r)\, d\vec{r} \quad (11a)$$

where A_o is the Helmholtz free energy of the athermal reference system of volume V, and $\beta = 1/k_BT$. If $\beta w_{\alpha\gamma}(r)$ is small, then first-order perturbation theory[29] implies that the radial distribution functions $g_{\alpha\gamma}(r)$ are not influenced by the attractive interactions and, to first order, can be replaced by the corresponding pair correlation functions $g^o_{\alpha\gamma}(r)$ of the athermal reference system determined in the previous section. Hence to first order the free energy is given by

$$\frac{\beta A}{V} = \frac{\beta A_o}{V} + \frac{1}{2}\sum_{\alpha\gamma}\varrho_\alpha\varrho_\gamma \int \beta w_{\alpha\gamma}(r)\, g^o_{\alpha\gamma}(r)\, d\vec{r} \quad (11b)$$

Equation 11b also applies to the pure component melts of PE and i-PP so that we can immediately write the melt free energy of our single D site model of PE as

$$\frac{\beta A^{\text{PE}}}{V} = \frac{\beta A_o^{\text{PE}}}{V} + 2\varrho_{\text{PE}}^2 \int \beta w_{\text{DD}}(r)\, g_{\text{DD}}^{\text{melt}}(r)\, d\vec{r} \quad (12a)$$

and the three (A, B, C) site model of i-PP free energy as

$$\frac{\beta A^{\text{PP}}}{V} = \frac{\beta A_o^{\text{PP}}}{V} + \frac{\varrho_{\text{PP}}^2}{2}\sum_{a,b=A}^{C} \int \beta w_{ab}(r)\, g_{ab}^{\text{melt}}(r)\, d\vec{r} \quad (12b)$$

In eqs 12 the site densities and radial distribution functions refer to the melt densities and athermal melt pair correlation functions. From eqs 11 and 12 we can now compute the Helmholtz free energy of mixing of the

blend according to

$$\Delta A_{\text{mix}} = A - \phi A^{\text{PE}} - (1 - \phi)A^{\text{PP}}$$
$$= \Delta E_{\text{mix}} - T\Delta S_{\text{mix}} \quad (13a)$$

where ϕ and $(1 - \phi)$ are the volume fractions of PE and i-PP, respectively, and ΔE_{mix} and ΔS_{mix} are the internal energy and entropy of mixing. Likewise the Gibbs free energy of mixing ΔG_{mix} at pressure P can be written as

$$\Delta G_{\text{mix}} = \Delta A_{\text{mix}} + P\Delta V_{\text{mix}}$$
$$= \Delta H_{\text{mix}} - T\Delta S_{\text{mix}} \quad (13b)$$

where $\Delta H_{\text{mix}} = \Delta E_{\text{mix}} + P\Delta V_{\text{mix}}$ is the enthalpy of mixing and ΔV_{mix} is the volume change on mixing at constant pressure P. The volume fractions are related to the monomer densities ϱ_{PE} and ϱ_{PP} through the identities

$$\phi = \frac{\varrho_{\text{PE}}\nu_{\text{PE}}}{\eta} \qquad (1 - \phi) = \frac{\varrho_{\text{PP}}\nu_{\text{PP}}}{\eta} \quad (14a)$$

In eq 14a ν_{PE} and ν_{PP} are the volumes of PE and i-PP monomers, respectively. η is the packing fraction defined as

$$\eta = \nu_{\text{PE}}\varrho_{\text{PE}} + \nu_{\text{PP}}\varrho_{\text{PP}} \quad (14b)$$

In general $\eta(\phi)$ would be expected to depend on composition in a manner that is determined by the equation-of-state of the blend. A common assumption, which we invoke here, neglects volume changes on mixing. Hence we make the approximation that $\Delta V_{\text{mix}} = 0$. This is equivalent to approximating the partial molar volumes by the molar volumes in the corresponding pure component melts. With this approximation we can demonstrate that for zero volume change on mixing the packing fraction is simply related to the pure component packing fractions η^o_{PE} and η^o_{PP}

$$\frac{1}{\eta(\phi)} = \frac{\phi}{\eta^o_{\text{PE}}} + \frac{(1 - \phi)}{\eta^o_{\text{PP}}} \quad (14c)$$

In the case of PE/i-PP the pure component densities or volume fractions are approximately equal.[40,41] With this further approximation the blend packing fraction in eq 14c becomes a constant $\eta \approx \eta^o_{\text{PE}}$. As illustrated in Figure 1, the monomers are constructed from overlapping hard sphere sites. From straightforward solid geometry calculations we can then estimate the required monomer volumes neglecting three-sphere (and higher) overlaps

$$\nu_{\text{PE}} = 2\nu \qquad \nu_{\text{PP}} = 3\nu \quad (15a)$$

where ν is the average volume of a single site

$$\nu = \left(\frac{\pi d^3}{6}\right)\left[\frac{3}{2}\left(\frac{L}{d}\right) - \frac{1}{2}\left(\frac{L}{d}\right)^3\right] \quad (15b)$$

L is the bond length (1.54 Å), and d is the diameter of the sites (assumed to be $d_{\alpha\gamma} = d = 3.9$ Å). The ratio η/ν is the average density of sites which we estimate to be 0.0313 Å^{-3} (0.7281 g/cm^3) on the basis the melt densities of polyethylene and polypropylene.

Since to first order the radial distribution functions of the blend are unaffected by the attractive potentials $\beta w_{\alpha\gamma}(r)$, then the entropy of mixing ΔS_{mix} is entirely determined from the purely repulsive, athermal, refer-

ence system. Likewise, the internal energy of mixing ΔE_{mix} arises from the attractive potentials, mediated by the local packing determined by the athermal, reference system. Using eqs 11–15, we can write the heat of mixing for the PP/i-PP blend under investigation in the form

$$\frac{\beta \Delta E_{\text{mix}}}{V} = \left(\frac{\eta}{\nu}\right) \chi_{\text{H}} \phi(1 - \phi) \qquad (16)$$

χ_{H} is an energetic χ parameter defined as

$$\chi_{\text{H}}(\phi) = -\frac{1}{2}\left(\frac{\eta}{\nu}\right)[\Delta H_{\text{PE}} + \Delta H_{\text{PP}} - 2\Delta H_{\text{PE/PP}}] \quad (17a)$$

$$\Delta H_{\text{PE}} = (1 - \phi)^{-1} \int \beta w_{\text{DD}}[g_{\text{DD}}^{\text{melt}} - \phi g_{\text{DD}}^{\circ}] \, d\vec{r} \quad (17b)$$

$$\Delta H_{\text{PP}} = \frac{1}{9\phi} \sum_{a,b=A}^{C} \int \beta w_{\text{ab}}[g_{\text{ab}}^{\text{melt}} - (1 - \phi)g_{\text{ab}}^{\circ}] \, d\vec{r} \quad (17c)$$

$$\Delta H_{\text{PE/PP}} = \frac{1}{3} \sum_{a=A}^{C} \int \beta w_{\text{aD}}g_{\text{aD}}^{\circ} \, d\vec{r} \qquad (17d)$$

A serious obstacle in describing the statistical mechanics of realistic polymer alloys is that the interatomic potentials are not accurately known. Even in polyolefins[39] the various site–site potentials among CH_2, CH_3, and CH moieties are not well characterized. We do, however, expect the Lennard-Jones attraction parameters $\epsilon_{\alpha\gamma}$ in eq 9 to be proportional to the polarizabilities of sites α and γ. In view of the definitions of the four sites used in constructing PE and i-PP, we can write the ten Lennard-Jones attractions in terms of only three independent parameters according to

$$\epsilon_{\text{AA}} = \epsilon_{\text{DD}} = \epsilon_{\text{AD}} = \epsilon$$

$$\epsilon_{\text{CC}} = \lambda_1^2 \epsilon \qquad \epsilon_{\text{BB}} = \lambda_2^2 \epsilon \qquad \epsilon_{\text{AB}} = \epsilon_{\text{BD}} = \lambda_2 \epsilon$$

$$\epsilon_{\text{AC}} = \epsilon_{\text{CD}} = \lambda_1 \epsilon \qquad \epsilon_{\text{BC}} = \lambda_1 \lambda_2 \epsilon \qquad (18a)$$

In this parameterization, ϵ is the attraction between pairs of methylene sites, λ_1 is the ratio of polarizabilities of a CH_3 to CH_2 site, and λ_2 is the corresponding polarizability ratio between CH and CH_2 sites.

$$\lambda_1 = \sqrt{\epsilon_{\text{CC}}/\epsilon_{\text{AA}}} \qquad \lambda_2 = \sqrt{\epsilon_{\text{BB}}/\epsilon_{\text{AA}}} \quad (18b)$$

For simplicity we will also approximate the Lennard-Jones σ parameters in eq 9 as being the same for all pairs of sites ($\sigma_{\alpha\gamma} = \sigma$).

From eqs 16 and 17 it can be seen that the heat of mixing is strongly influenced by the intermolecular packing expressed by the pair correlation functions $g_{\alpha\gamma}^{\circ}(r)$. Because the intersite attractions $w_{\alpha\gamma}(r)$ are short range functions, the range of the integrations in eqs 17 is effectively cut off at very short distances. Thus it is only the short range, nonuniversal aspects of $g_{\alpha\gamma}^{\circ}(r)$ that contribute to the heat of mixing and enthalpic χ parameter. In Flory–Huggins theory[9] the random mixing approximation is made. In our language this is equivalent to replacing each of the $g_{\alpha\gamma}^{\circ}(r)$ by 1. In this random mixing limit, together with the parameterization in eq 18, the enthalpic χ parameter in eq 17 considerably simplifies to give the continuum analog of the Flory–Huggins χ parameter χ_{FH} for our four-site model of the PE/i-PP blend.

$$\chi_{\text{FH}} = \frac{16\pi\beta\epsilon\sigma^3}{9}\left(\frac{\eta}{\nu}\right)\left(\frac{1 + \lambda_1 + \lambda_2}{3} - 1\right)^2 \quad (19)$$

In this investigation we will examine the effects of nonrandom, local packing on the miscibility of the PE/i-PP mixture. Thus it will be instructive to compare the critical temperatures computed from the detailed PRISM calculations carried out here, with the corresponding T_c from the continuum Flory–Huggins model.

B. Entropy of Mixing. In order to complete the calculation of the phase diagram of the polyolefin mixture we now address the effect of intermolecular packing on the entropy of mixing of the athermal system. The Helmholtz free energy for the athermal blend can be written in the convenient form[24]

$$dA_o = -SdT + PdV + \eta V\left(\frac{\mu_{\text{PE}}}{N_{\text{PE}}\nu_{\text{PE}}} - \frac{\mu_{\text{PP}}}{N_{\text{PP}}\nu_{\text{PP}}}\right)d\phi \quad (20)$$

where μ_{α} is the chemical potential of either polymer species. Since in the athermal mixture the heat of mixing is zero we can write the Helmholtz free energy of mixing as

$$\Delta A_{\text{o mix}} = -T\Delta S_{\text{mix}} \qquad (21)$$

The partial structure factors $\hat{S}_{\alpha\gamma}(k)$, defined in eqs 7 and 8, are conveniently obtainable from PRISM theory through the direct correlation functions. In the thermodynamic limit of zero wave vector ($k \rightarrow 0$), the partial structure factors are related to the osmotic compressibility of the blend and provide us a convenient link between PRISM theory and thermodynamics. Following Kirkwood and Buff,[43] it is possible to express the chemical potentials of the two-component mixture in terms of the zero wave vector structure factors. This leads, using eq 20 and 21, to the following expression for the entropy of mixing:

$$\left(\frac{\partial^2 \Delta S_{\text{mix}}}{\partial \phi^2}\right)_{TP} =$$

$$\frac{-k_{\text{B}}(\eta/\nu)^2 V}{[9\phi^2\hat{S}_{\text{AA}}(0) - 6\phi(1 - \phi)\hat{S}_{\text{AD}}(0) + (1 - \phi)^2\hat{S}_{\text{DD}}(0)]} \quad (22)$$

In eq 22 the $\hat{S}_{\alpha\gamma}(0)$ are the elements of the 4 × 4 structure factor matrix from eq 8 at zero wave vector. The isothermal compressibility κ_T can also be expressed for our case in terms of $\hat{S}_{\alpha\gamma}(0)$ using the general formulation of Kirkwood and Buff[43]

$$k_{\text{B}}T\kappa_T =$$

$$\frac{9(\nu/\eta)^2[\hat{S}_{\text{AA}}(0)\,\hat{S}_{\text{BB}}(0) - \hat{S}_{\text{DD}}^2(0)]}{[9\phi^2\hat{S}_{\text{AA}}(0) - 6\phi(1 - \phi)\hat{S}_{\text{AD}}(0) + (1 - \phi)^2\hat{S}_{\text{DD}}(0)]} \quad (23)$$

The Flory–Huggins theory makes the assumption of incompressibility for which $\kappa_T \rightarrow 0$, a condition which does not exist in real systems. In this limit of a hypothetical incompressible system the constant pressure derivative in eq 22 is equivalent to the corresponding derivative at constant volume.

$$\left(\frac{\partial^2 \Delta S_{\text{mix}}}{\partial \phi^2}\right)_{TV} =$$

$$\frac{-k_{\text{B}}(\eta/\nu)^2 V[9\hat{S}_{\text{AA}}(0) + 6\hat{S}_{\text{AD}}(0) + \hat{S}_{\text{DD}}(0)]}{[\hat{S}_{\text{AA}}(0)\,\hat{S}_{\text{DD}}(0) - \hat{S}_{\text{AD}}^2(0)]} \quad (24)$$

It is important to note that the site index A in eqs 22–24 could equally well be replaced by either a B or C index. This follows because the six partial structure factors associated with the i-PP monomer can be shown to be identical in the zero wave vector limit. In addition, the Flory–Huggins theory also makes the random mixing approximation which, in our language, can be stated as $g_{\alpha\gamma}(r) = 1$ or $\hat{h}_{\alpha\gamma}(k) = 0$. For our system this implies that

$$\hat{S}_{AA}(0) = \varrho_A N_A \qquad \hat{S}_{DD}(0) = \varrho_D N_D$$
$$\hat{S}_{AD}(0) = 0 \qquad \text{(random mixing)}$$

If these random mixing conditions are enforced in eq 24, we then recover the Flory–Huggins or RPA expression for our system.

$$\left(\frac{\partial^2 \Delta S_{\text{mix}}}{\partial \phi^2}\right)_{TV} = -k_B\left(\frac{\eta}{\nu}\right)V\left[\frac{1}{2N_{\text{PE}}\phi} + \frac{1}{3N_{\text{PP}}(1-\phi)}\right] \quad (25a)$$

One can then define an athermal χ parameter, related to the noncombinatorial entropy of mixing, as follows:

$$2\frac{\eta}{\nu}\chi_{\text{ath}} = \frac{\eta}{\nu}\left[\frac{1}{2\phi N_{\text{PE}}} + \frac{1}{3(1-\phi)N_{\text{PP}}}\right] + \frac{T}{V}\left(\frac{\partial^2 \Delta S_{\text{mix}}}{\partial \phi^2}\right)_{TP} \quad (25b)$$

This definition is analogous to the SANS χ parameter frequently used to interpret neutron scattering experiments on polymer blends. Thus in the Flory–Huggins limit the athermal χ parameter is defined to be zero. Note that the first term on the right hand side of eq 25 diverges in the pure component limits ($\phi \to 0$, 1). Therefore, unless the second term also diverges in the same way

$$\frac{-\nu T}{V\eta}\left(\frac{\partial^2 \Delta S_{\text{mix}}}{\partial \phi^2}\right)_{TP} \sim \frac{1}{\phi N_{\text{PE}}} \quad \text{and} \quad \frac{1}{(1-\phi)N_{\text{PP}}}$$

then the athermal χ parameter will also, by definition, diverge in the pure component limits. Thus, there may be an apparent composition dependence in χ_{ath} which is merely caused by the divergences inherent in its definition.

Equation 25a can then be used with eq 19 for the enthalpic χ parameter to compute the spinodal temperature T_s in the Flory–Huggins theory, which enforces both the incompressibility and the random mixing approximations.

$$T_S = \frac{16(\epsilon/k_B)\pi\sigma^3}{9\left[\frac{1}{4\phi N_{\text{PE}}} + \frac{1}{6(1-\phi)N_{\text{PP}}}\right]}\left(\frac{\eta}{\nu}\right)\left(\frac{1 + \lambda_1 + \lambda_2}{3} - 1\right)^2 \quad (25c)$$

For the case considered here, in which there are three independent polypropylene sites and two equivalent polyethylene sites per monomer, the critical composition (obtained by setting the composition derivative of eq 25c to zero) is 0.55.

The effect of nonrandom intermolecular packing on the entropy of mixing is contained in the zero wave vector structure factors in eq 22. We have calculated the entropy of mixing second derivative in eq 22 for an athermal blend having degrees of polymerization $N_{\text{PE}} = N_{\text{PP}} = 200$ from PRISM theory using the information described in section II. These results are shown in
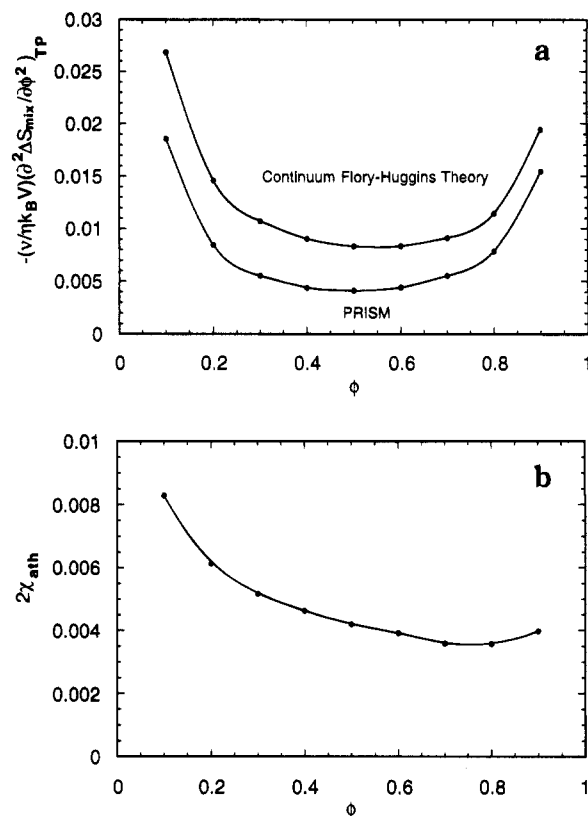
Figure 6. (a) Second derivative of the entropy of mixing for the athermal blend of PE/i-PP ($N_{\text{PE}} = N_{\text{PP}} = 200$). The lower curve is from a PRISM calculation using eq 22. The upper curve is the result for the continuum Flory–Huggins theory, eq 25a, assuming random mixing ($g_{\alpha\gamma}(r) = 1.0$). (b) Athermal χ parameter calculated from PRISM theory using eq 25b as a function of the volume fraction of polyethylene. The random mixing, Flory–Huggins theory gives $\chi_{\text{ath}} = 0$.

Table 1. Van der Waals Energies[44,45] for PE/i-PP

|	Small	Hoy	Van Krevelen	Jorgensen
$\lambda_1 = \sqrt{\epsilon_{CC}/\epsilon_{AA}}$	1.61	1.13	1.5	1.22
$\lambda_2 = \sqrt{\epsilon_{BB}/\epsilon_{AA}}$	0.21	0.65	0.5	0.71
$[((1 + \lambda_1 + \lambda_2)/3) - 1]^2$	0.0036	0.0054	0.0	0.00071

Figure 6a along with the corresponding Flory–Huggins, random mixing limit obtained from eq 25a. It can be observed that the intermolecular packing correlations have the effect of reducing the entropy of mixing relative to the Flory–Huggins theory. In Figure 6b we have plotted the athermal χ parameter computed from eqs 22 and 25b.

IV. Results and Discussion

In this work we want to explore the effect of local intermolecular packing on the phase behavior of the PE/i-PP blend. Unfortunately, the polarizability ratios λ_1 and λ_2 reported in the literature for alkanes vary from one study to the next.[44] Because of this uncertainty, we decided to perform PRISM calculations for various sets of λ_1 and λ_2 and then compare with the corresponding Flory–Huggins predictions for the same set of parameters.

Jorgensen and co-workers[44] obtained the Lennard-Jones parameters for various alkanes by comparing thermodynamic predictions based on Monte Carlo simulation with experimental data. We estimated λ_1 and λ_2 based on the Jorgensen data; the results are shown in Table 1. Another way to estimate the polarizability ratios is to use the group contribution tables for solubil-
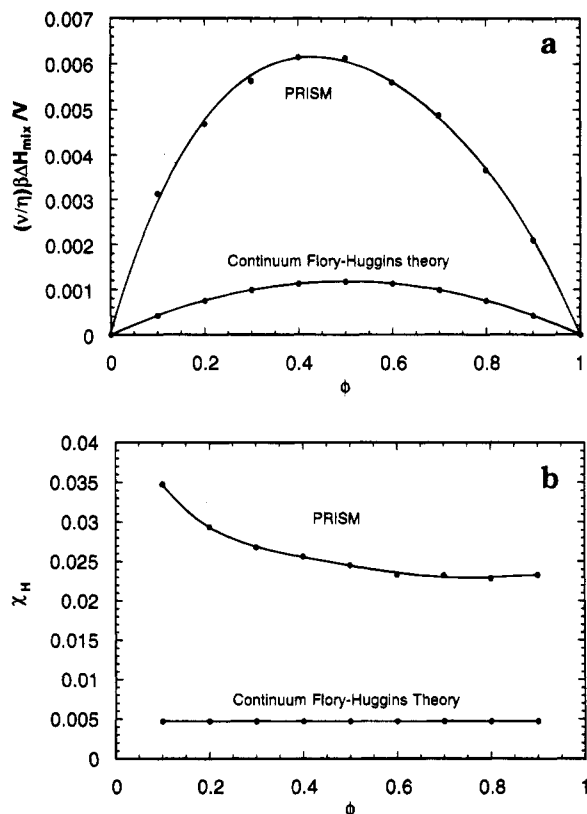
Figure 7. (a) Heat of mixing of the PE/i-PP ($N_{PE} = N_{PP} = 200$) blend as a function of composition using the polarizability ratios λ_1 and λ_2 estimated from the solubility parameter group contributions of Small.[45] The upper curve is from PRISM theory using eqs 16 and 17. The lower curve is the continuum Flory–Huggins theory, eq 19, assuming random mixing ($g_{\alpha\gamma}(r) = 1.0$). (b) Enthalpic χ parameters as a function of composition corresponding to the conditions in Figure 7a.

ity parameters.[45] In this estimate we assumed that the molar volumes of the CH_3, CH_2, and CH species were equal. This assumption leads to three additional sets of λ_1 and λ_2 also listed in Table 1. In Table 1 the third row lists a "contrast factor" based on the Flory–Huggins χ parameter in eq 19. A contrast factor of zero corresponds to a zero Flory–Huggins χ parameter.

We computed the heat of mixing of the various blends in Table 1 from eqs 16 and 17 as a function of composition and the dimensionless temperature $T^* = k_BT/\epsilon$. Typical results are shown in Figure 7a at $T^* = 11.1$ for the set of λ_1 and λ_2 based on Small's group contributions.[45] Also shown in Figure 7a is the corresponding continuum Flory–Huggins prediction based on eq 19. It can be seen from this figure that the PRISM theory gives much higher heats of mixing than Flory–Huggins theory. This is a consequence of the local intermolecular packing of the monomers in the PE/i-PP blend. For example, the contribution to ΔE_{mix} of the methyl–methyl interactions, which are larger than the corresponding methylene–methylene potential, are further enhanced because methyl groups are not screened and can approach each other more readily than methylene groups on the chain backbone. Likewise the small CH/CH interactions are de-emphasized because of the large screening of backbone CH sites in polypropylene. Thus the net effect of the subtle packing in this blend leads to a larger heat of mixing and to a corresponding destabilization of the mixture relative to Flory–Huggins theory which assumes random mixing. In order to capture these nonuniversal packing effects a molecularly realistic, multisite PRISM model, together

with a realistic accounting of the chain architecture in the intramolecular structure functions $\hat{\Omega}_{\alpha\gamma}(k)$, would be expected to be necessary. Such local packing information is not available from coarse-grained models.[13]

In Figure 7b we represent the heat of mixing data by the enthalpic χ parameter from eq 17. Note that there is a significant asymmetric composition dependence to the χ_H obtained from PRISM theory. We see that the local, nonrandom packing effects lead to an enthalpic χ parameter approximately 5–7 times larger than the corresponding Flory–Huggins χ with the same energetic parameters.

From our perturbation theory approach, we can now construct the free energy of mixing in terms of the enthalpic and athermal χ parameters

$$\frac{\beta\Delta G_{mix}}{V} = \frac{\eta}{\nu}\left[\frac{\phi\ln\phi}{2N_{PE}} + \frac{(1-\phi)\ln(1-\phi)}{3N_{PP}}\right] +$$

$$\frac{\eta}{\nu}\chi_H(\phi)\,\phi(1-\phi) - 2\frac{\eta}{\nu}\int_0^\phi d\phi'\int_{1/2}^{\phi'}\chi_{ath}(\phi'')\,d\phi'' +$$

$$\frac{\beta P}{V}\Delta V_{mix} \quad (26)$$

Recall that we are neglecting the volume change on mixing or "equation-of-state effects" by neglecting ΔV_{mix} in eq 26. In principle, eq 26 could be used, in conjunction with the composition dependence of the two χ parameters, to compute the chemical potentials and hence the binodal phase diagram for our system. For computational simplicity, in the present study we will instead compute the spinodal curve which is obtained through the relation

$$\frac{\beta\nu}{V\eta}\left(\frac{\partial^2\Delta G_{mix}}{\partial\phi^2}\right)_{TP} = \left[\frac{1}{2\phi N_{PE}} + \frac{1}{3(1-\phi)N_{PP}}\right] - 2\chi_{ath} +$$

$$\left(\frac{\partial^2\chi_H\phi(1-\phi)}{\partial\phi^2}\right)_{TP}$$

$$= 0 \quad (27)$$

The athermal terms in eq 27 were obtained directly from Figure 6a as a function of composition. The heat of mixing was fit to a fourth-order polynomial and is shown as the upper curve in Figure 7a; the required second derivative was then easily obtained as a quadratic function of composition. The resulting compositions at various reduced temperatures $T^* = k_BT/\epsilon$, which satisfy eq 27, are plotted as the spinodal curve in Figure 8 along with the Flory–Huggins prediction. It can be observed from this figure that the PRISM theory predicts that the PE/i-PP blend is considerably more unstable than predicted by Flory–Huggins theory. For the case plotted in Figure 8 the critical temperature is approximately 12 times higher. Other numerical procedures were also employed in approximating the second derivative term in eq 27 with essentially the same result.

In order to convert the reduced temperatures in Figure 8 into real temperature units we need to estimate the Lennard-Jones parameter ϵ between pairs of methylene groups. From earlier work[46] on calculation of the equation-of-state of polyethylene melts it was found that $\sigma = 4.36$ Å and $\epsilon/k_B \approx 42$ K. From this we conclude from re-examination of Figure 8 that the PE/i-PP blend of 200 monomer units has no miscibility under experimentally relevant conditions. This is qualitatively consistent with experimental observations,
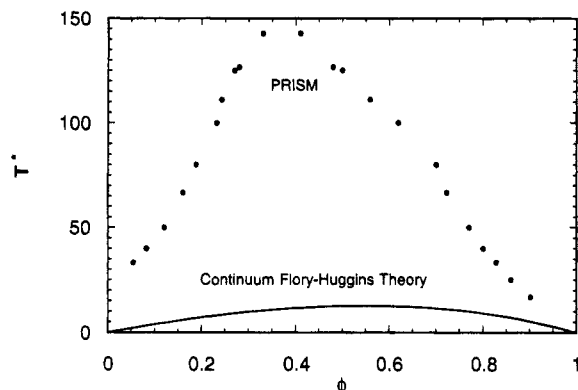
Figure 8. Predicted spinodal curve for the PE/i-PP (N_{PE} = N_{PP} = 200) blend as a function of composition using the polarizability ratios λ_1 and λ_2 estimated from the solubility parameter group contributions of Small.[45] The upper points correspond to the PRISM prediction; the lower curve is the corresponding continuum Flory–Huggins prediction assuming random mixing. $T^* = k_B T/\epsilon$ is the dimensionless temperature reduced by ϵ, the Lennard-Jones attraction parameter between a pair of CH_2 groups.

Table 2. Estimated Critical Temperatures ($T_c^* = k_B T_c/\epsilon$), $N = 200$

	Small	Hoy	Van Krevelen	Jorgensen
lattice				
Flory–Huggins	12	16	0.2	n/a
continuum				
Flory–Huggins	13	19	0	2
PRISM	148	134	30	37

indicating a high degree of incompatibility in this blend. Figure 8 depicts the spinodal curve for the polarizability ratios λ_1 and λ_2 estimated from group contributions tabulated by Small.[45] Qualitatively similar conclusions were observed from the other λ_1 and λ_2 sets listed in Table 1. The approximate critical temperatures for all cases studied are summarized in Table 2. T_c^* estimates from the continuum Flory–Huggins treatment in eq 25c and from the standard lattice Flory–Huggins treatments[9,45] are also presented in Table 2.

It can be observed in Table 2 that there is considerable variation in the estimated reduced critical temperatures depending on which set of polarizability ratios are used. This emphasizes the need for improved united atom force fields; better estimates of λ_1 and λ_2 are in principle possible from quantum mechanical calculations or experiment. Nevertheless, the qualitative trends in Table 2 are consistent. PRISM theory predicts that the PE/i-PP mixture is considerably more immiscible than predicted by Flory–Huggins theory and provides a rationale for available experimental observations on PE/i-PP blends. PRISM theory even predicts immiscibility for the Van Krevelen estimates of the polarizability ratios for which there is zero net contrast in the continuum Flory–Huggins estimate. Thus it appears that subtle, local packing information, controlled by the detailed chemical structure of the polymer chains, plays a crucial role in determining the miscibility behavior of the PE/i-PP system.

The example studied in the present investigation was for degrees of polymerization $N = N_{PE} = N_{PP} = 200$. Higher molecular weights could likewise be studied using the same methods employed here. The definition of the athermal χ parameter in eq 25b suggests that χ_{ath} would decrease with increasing degree of polymerization. Such trends have been observed in coarse-grained PRISM treatments.[14] On the other hand one can argue

that the enthalpic χ parameter from eqs 17 would saturate (along with the local pair correlation functions) to a constant value at large degrees of polymerization. Thus the perturbation theory approach that we introduce here would be expected to display classical scaling of the critical temperature $T_c \sim N$ with molecular weight.

We remind the reader that in the present analysis we neglect equation-of-state effects and assume that the volume change on mixing is zero. It is important to recognize that this does not imply the mixture is incompressible, for which the isothermal compressibility in eq 23 is zero. The further assumption of incompressibility, which we do not employ here, would lead one to use thermodynamic derivatives under a constant volume constraint, as in eq 25a. Measurements of the volume changes on mixing suggest that ΔV_{mix} is a small number of polyolefins, but it is difficult to assess the consequences of assuming it is zero on the phase diagram. In principle, this assumption could be relaxed and the equation-of-state for the mixture and pure components could be extracted from the PRISM analysis.

V. Conclusions

In the present investigation we have outlined an integral equation theory for the intermolecular packing, thermodynamics, and miscibility of polyolefin and related blends. In this approach we use thermodynamic perturbation theory to treat the thermodynamics of the actual (thermal) blend with attractive interactions. The athermal mixture serves as the reference system and is analyzed using PRISM theory with purely repulsive interactions for which the PY closure is applicable. In this treatment we expect that at high molecular weight the spinodal temperature will exhibit classical scaling with molecular weight.

The approach was illustrated with detailed calculations on the PE/i-PP mixture where each component contains 200 monomers. The results based on PRISM theory indicate that nonuniversal, local intermolecular correlations play a crucial role in determining the miscibility of the mixture. Both the heat and entropy of mixing showed significant deviations from continuum Flory–Huggins theory. Similar calculations on other polyolefin blend systems are currently in progress.

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