Macromolecules **2000,** *33,* 3467−3477

Lattice Cluster Theory for Pedestrian. 2. Random Copolymer Systems

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Received October 19, 1999; Revised Manuscript Received January 18, 2000

ABSTRACT: An analytically tractable, more realistic extension of random copolymer Flory−Huggins (FH) theory is developed for A_xB_{1-x}/C_yD_{1-y}, A_xB_{1-x}/A_yB_{1-y}, and A/C_yD_{1-y} random copolymer binary blends. The theory describes the polymer−polymer interactions in terms of the interactions between united atom groups and includes a temperature-independent contribution χ_s to the effective interaction parameter χ. χ_s is determined (with no adjustable parameters) from the lattice cluster theory in the incompressible, athermal, fully flexible, long-chain limit. The general, readily applied expressions for the interaction parameter χ are illustrated for norbornene-*co*-ethylene (N_xE_{1-x}/N_yE_{1-y}) random copolymer mixtures for which the theory has been successfully used by Delfolie et al. (*Macromolecules* **1999**, *32*, 7781) to explain miscibility data that depart significantly from the predictions of classic random copolymer FH theory. Further illustrations describe the influence of chain semiflexibility and sequence dependence on the miscibility of N_xE_{1-x}/N_yE_{1-y} blends. The theory is then applied to isotopic mixtures of saturated poly(butadienes) (sPB) whose randomness stems from the random addition of 1,2 and 1,4 units in the polymerization process. A final application treats blends of ethylene-*co*-α-alkene random copolymers with sPB.

I. Introduction

Random copolymer systems are of considerable technological and scientific importance. The earliest theoretical descriptions[1−5] for these systems are based on a direct extension[6,7] of Flory−Huggins theory to random copolymers. While the random copolymer FH theory has been very successful in explaining the enhanced miscibilities observed[2−4] in many systems containing random copolymers, the theory exhibits some serious limitations. First of all, the theory is insensitive to monomer sequence and to the detailed chemical structure of the individual monomers. Some attempts[8−10] toward improving the random copolymer FH theory introduce a set of phenomenological interaction parameters $\chi_{ijk,lmn}$ (or $\chi_{ij,kl}$) that explicitly depend on the monomer sequence. However, these phenomenological models are required to invoke additional (often arbitrary) assumptions to reduce the huge number of resulting $\chi_{ijk,lmn}$ parameters to a manageable few. Thus, there is a great need for developing analytically simple, more realistic, improved theories with a minimal number of adjustable parameters. These improved, yet simple theories should provide an adequate tool for probing general physical trends. An example of these types of simple, molecular-based theories is given by the "pedestrian" version of the lattice cluster approach for binary homopolymer blends.[11] The present paper develops a simpler, but more approximate pedestrian lattice cluster theory (LCT) for random copolymer systems, with particular applications to blends containing random copolymer polyolefins.

In addition to the immense technological importance of polyolefins and to the enormous progress[12,13] in their synthesis that enables the control of their chemical structures, binary blends of polyolefins represent a class of "weakly interacting" systems for which our previous works predict[14] that slight modifications of chemical structure, e.g., shifting the position of methyl side groups, can significantly alter the properties of the blends. Experiments by Graessley and co-workers[15] exemplify our earlier predictions[14] by exhibiting, for example, considerably different miscibilities of ordinary head-to-tail poly(propylene) and head-to-head poly(propylene) with other polyolefins, a remarkable feature recently explained[16] on a molecular basis by the pedestrian LCT, along with an explanation of several other examples of anomalous mixing occurring in these systems.[11,16] A large body of experimental data[15,17,18] for polyolefin blends displays a similar strong dependence of thermodynamic properties on monomer molecular structures, and the explicit details and trends remain to be understood within a molecular context. The majority of these data pertain to blends in which one or both of the components are random copolymers, systems quite prevelant in technological applications. Because a complete random copolymer extension[19] of the LCT is *extremely* lengthy and algebraically very complicated, our goal here lies in developing useful simplified limits of the random copolymer LCT that are easily applied by experimentalists[11,16] and that can still distinguish between the chemical structures of various systems. This pedestrian random copolymer theory is likewise applied here to particular random copolymer polyolefin blends that display trends departing from the predictions of random copolymer FH theory.[11,16]

Both classic FH theory and its extension to random copolymer systems[6,7] employ an effective interaction parameter χ that emerges from FH theory as a purely enthalpic quantity. However, as reviewed by Flory 30 years ago,[20] the prevalence of systems with a temperature-independent portion of χ requires introduction of this "entropic" portion χ_s into FH theory as necessary empiricism devoid of theoretical basis (at that time but explained by us[11]). A similar situation exists for the widely used solubility parameter theory that formally relates the χ parameters to the internal energy, and, therefore, the definition of the solubility parameter does not contain athermal packing entropy contributions to χ, contributions that Flory notes often dwarf the enthalpic portions (e.g., for polymer solutions). Thus, applications of solubility parameter theory, in effect, can only include χ_s as pure phenomenology that conflicts

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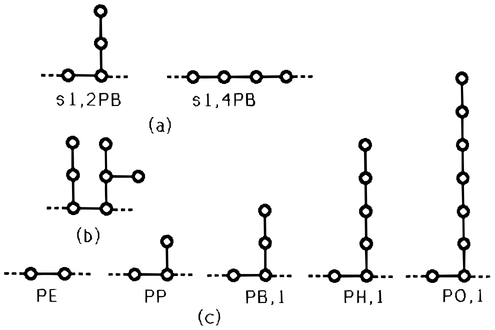

Figure 1. United atom structures used for (a) saturated 1,2 and 1,4 poly(butadiene) (sPB) units, (b) the norbornene (N) monomer, and (c) poly(ethylene) (PE), poly(propylene) (PP), poly(butene-1) (PB1), poly(hexene-1) (PH1), and poly(octene-1) (PO1) monomers. Each united atom group comprises a carbon atom with its directly bonded hydrogens.

with the basic assumptions of solubility parameter theory. On the other hand, LCT is free of this serious deficiency. Both the entropic and enthalpic contributions to χ emerge naturally from the LCT free energy and from the underlying extended lattice model that allows monomers of different polymer species to have different shapes, sizes, and interactions.[11]

The present work provides a theory which appends the LCT description[14] of the athermal limit noncombinatorial entropy to the extension[6,7] of random copolymer FH theory to model the polymer−polymer interactions in terms of the more realistic interactions between united atom groups. Particularly compact analytical expressions are derived for the (composition-independent) effective interaction parameter χ appropriate to A_xB_{1-x}/A_yB_{1-y}, A_xB_{1-x}/C_yD_{1-y}, and A/C_yD_{1-y} random copolymer binary blends. This new work and prior LCT treatments of homopolymer blends further suggest modifications of solubility parameter theories by augmenting the enthalpic χ (determined from solubility parameter theory) with the entropic portion χ_s evaluated, for instance, from LCT.

The general theory of section II is illustrated first in section III for binary blends of norbornene-*co*-ethylene random copolymers, a system for which the theory has been applied by Delfolie and co-workers[1] to describe miscibility data that significantly deviate from predictions of standard random copolymer FH theory. The analysis also explains how to incorporate the influence of rigidity in the norbornene side groups and of steric interactions between bonded norbornene monomers on the miscibility of these systems. Another application of the theory in section IV concerns the “deuterium swap effect” in isotopic mixtures of saturated poly(butadienes) (sPB), where one component is hydrogenated while the other is partially deuterated.[21] Both components are random copolymers because of the presence of varying degrees of 1,2 and 1,4 units. Figure 1a depicts the quite obvious united atom monomer structures used for the 1,2 and 1,4 substitution monomers. Finally, the theory is applied in section V to blends of ethylene-*co*-α-alkene and sPB random copolymers to demonstrate the utility of the simple entropic structural parameter in predicting general miscibility trends.

II. Random Copolymer Theory with Entropic Terms

Random copolymer FH theory[6] is generalized here based on two significant molecular improvements. The first improvement lies in the description of the polymer−polymer interactions in terms of the united atom groups that are used to represent the monomer structures, an approach that is chemically more realistic than the traditional FH model based on monomer−monomer interactions. In addition, the theory is augmented[19,22] with entropic contributions to the interaction parameters χ_{ij}. These temperature-independent portions of χ_{ij} are completely determined by the monomer molecular structures and the copolymer compositions within the infinite pressure, fully flexible, long-chain limit of the random copolymer LCT. The entropic contributions to $\chi_{i,j}$ are evaluated here simply by counting[23] the numbers of various types of united atom groups (e.g., tri- and tetrafunctional groups) in the monomer structures such as those depicted in Figure 1.

The modified specific FH Helmholtz free energy f for a binary incompressible A_xB_{1-x}/C_yD_{1-y} random copolymer blend emerges in the apparently familiar form

$$\frac{f}{kT} = \frac{\phi_1}{M_1}\ln\phi_1 + \frac{\phi_2}{M_2}\ln\phi_2 + {\phi_1}^2\chi_{11} + {\phi_2}^2\chi_{22} + \phi_1\phi_2\chi_{12} \tag{1}$$

where k is Boltzmann’s constant, T designates the absolute temperature, ϕ_i is the volume fraction of species i ($\phi_1 + \phi_2 = 1$), and M_1 and M_2 are the numbers of lattice sites occupied by chains of each species. The M_α values are related to the average numbers n_α of α-type monomer units of species A and B in individual random copolymer chains 1 through the simple equation

$$M_1 = n_A s_A + n_B s_B \tag{2}$$

and of species C and D in chains 2 by

$$M_2 = n_C s_C + n_D s_D \tag{3}$$

with the monomer occupancy index s_α (α = A, B, C, D) equal to the number of lattice sites occupied by a single α monomer. The interaction parameters χ_{ij} of eq 1 are obtained from the molecular-based random copolymer theory as

$$\chi_{11} = -\frac{z}{2}\left[\frac{\epsilon_{AA}}{kT}{m_A}^2 + \frac{\epsilon_{BB}}{kT}{m_B}^2 + 2\frac{\epsilon_{AB}}{kT}m_Am_B\right] - \frac{1}{z^2}\left(\frac{N_2^{(1)}}{M_1}\right)^2 \tag{4}$$

$$\chi_{22} = -\frac{z}{2}\left[\frac{\epsilon_{CC}}{kT}{m_C}^2 + \frac{\epsilon_{DD}}{kT}{m_D}^2 + 2\frac{\epsilon_{CD}}{kT}m_Cm_D\right] - \frac{1}{z^2}\left(\frac{N_2^{(2)}}{M_2}\right)^2 \tag{5}$$

and

$$\chi_{12} = -z\left[\frac{\epsilon_{AC}}{kT}m_Am_C + \frac{\epsilon_{BD}}{kT}m_Bm_D + \frac{\epsilon_{AD}}{kT}m_Am_D + \frac{\epsilon_{BC}}{kT}m_Bm_C\right] - \frac{2}{z^2}\left(\frac{N_2^{(1)}}{M_1}\frac{N_2^{(2)}}{M_2}\right) \tag{6}$$

where the ratios

$$m_A = 1 - m_B \equiv \frac{n_A s_A}{M_1} = \frac{x s_A}{x s_A + (1-x) s_B} \tag{7}$$

and

$$m_C = 1 - m_D \equiv \frac{n_C s_C}{M_2} = \frac{y s_C}{y s_C + (1-y) s_D} \tag{8}$$

designate the fractions of single-chain lattice site occupancy indices M_1 and M_2 that are covered by monomers of species A and C, respectively, $x = n_A/(n_A + n_B)$ and $y = n_C/(n_C + n_D)$ denote the molar compositions of chains A_xB_{1-x} and C_yD_{1-y}, respectively, z is the lattice coordination number (taken as six for a cubic lattice),[24] $\epsilon_{\alpha\beta}$ (α, β = A, B, C, D) are monomer-averaged nearest-neighbor van der Waals attractive energies between united atom groups of species α and β, and the counting indices $N_2^{(i)}$ (i = 1, 2) for two sequential bonds in a single chain of species i are presented below as very simple functions of the fractions of tri- and tetrafunctional united atom units in chains of species i (i = 1, 2).

The novel features, distinguishing eqs 4−6 from the definitions of χ_{ij} in standard random copolymer FH theory,[6] are the appearance of the site occupancy fractions m_A and m_C, instead of only the chain compositions x and y, and the presence of the temperature-independent terms $(1/z^2)(N_2^{(i)}/M_i)(N_2^{(j)}/M_j)$. These new temperature-independent terms represent the influence of chain connectivity on the nonrandom chain packing and emerge[25] from the random copolymer LCT as the leading contributions to χ_{ij} in the incompressible, athermal, high molecular weight, fully flexible chain limit ($P \to \infty$, $T \to \infty$, $M_1 \to \infty$, $M_2 \to \infty$). The random copolymer LCT also contains corrections to the energetic portions of χ_{ij} in eqs 4−6, but these are presently unavailable for binary blends of random copolymers in a readily usable simple analytical form even for the high-pressure, high molecular weight limit that is used in deriving the athermal entropic corrections included in eqs 4−6.

The ratios $r_i = N_2^{(i)}/M_i$, i = 1, 2, are called partial entropic structural parameters and can be expressed[23] in terms of the numbers $s_i^{(\mathrm{tri})}$ and $s_i^{(\mathrm{tetr})}$ of tri- and tetrafunctional united atom units, respectively, in single monomers of species i.[26] The LCT for binary homopolymer polyolefin blends yields r_i for homopolymer chains of species 1 and 2 as[11]

$$r_i \equiv \frac{N_2^{(i)}}{M_i} = 1 + \frac{s_i^{(\mathrm{tri})}}{s_i} + \frac{3 s_i^{(\mathrm{tetr})}}{s_i}, \qquad i = 1, 2 \tag{9}$$

with s_i the monomer site occupancy index defined above. Reference 11 provides an extensive table of partial entropic structural parameters for a wide range of monomer structures, along with a limited discussion of how r_i may be modified to account for chain semiflexibility. The application of the general LCT expression in eq 9 to A_xB_{1-x}/C_yD_{1-y} systems produces the parameters r_i as dependent, in addition, on the composition variables x (or y)

$$r_1 \equiv \frac{N_2^{(1)}}{M_1} = \frac{[s_A + s_A^{(\mathrm{tri})} + 3s_A^{(\mathrm{tetr})}]x + [s_B + s_B^{(\mathrm{tri})} + 3s_B^{(\mathrm{tetr})}](1-x)}{s_A x + s_B(1-x)} \tag{10}$$

$$r_2 \equiv \frac{N_2^{(2)}}{M_2} = \frac{[s_C + s_C^{(\mathrm{tri})} + 3s_C^{(\mathrm{tetr})}]y + [s_D + s_D^{(\mathrm{tri})} + 3s_D^{(\mathrm{tetr})}](1-y)}{s_C y + s_D(1-y)} \tag{11}$$

At this stage, the theory is incapable of distinguishing random copolymers from block or alternating copolymers with the same compositions but is capable of distinguishing monomer structures, a feature that is responsible for the presence of temperature-independent terms in χ_{ij}. As shown previously,[27] the dependence on monomer sequence enters into the athermal limit entropy only as $1/M$ corrections which are neglected here. Order M^0 differences between random copolymers and block copolymers (of the same compositions) arise from nonathermal, nonrandom mixing effects, corrections which are also ignored in the present model because of their extreme analytical complexity.

The small-angle neutron scattering (SANS) monomer−monomer χ parameter is defined through the derivative of the free energy f as

$$\chi_{\mathrm{SANS}} = \sqrt{s_1 s_2}\,\frac{1}{2}\left[\frac{1}{M_1\phi_1} + \frac{1}{M_2\phi_2} - \left.\frac{\partial^2[f/kT]}{\partial {\phi_1}^2}\right|_{V,T}\right] \tag{12}$$

where $s_1 = s_A x + s_B(1-x)$ and $s_2 = s_C y + s_D(1-y)$ are the averaged monomer site occupancy indices for the A_xB_{1-x} and C_yD_{1-y} chains, respectively, and $\sqrt{s_1 s_2}$ is a conversion factor to transfer the LCT χ, which is computed on a lattice site basis, to an interaction parameter χ_{SANS} per monomer. After some lengthy algebra, eq 12 takes the form

$$\begin{aligned}\chi_{\mathrm{SANS}} &= -\sqrt{s_1 s_2}[\chi_{11} + \chi_{22} - 2\chi_{12}] \\ &= \sqrt{s_1 s_2}\Big\{\frac{1}{z^2}(r_1 - r_2)^2 + \frac{1}{s_1 s_2}[\chi_{AC} x y s_A s_C + \\ &\qquad \chi_{BC}(1-x)\, y s_B s_C + \chi_{AD} x(1-y)\, s_A s_D + \\ &\qquad \chi_{BD}(1-x)(1-y)\, s_B s_D - \chi_{AB} x(1-x) \times \\ &\qquad s_A s_B s_2/s_1 - \chi_{CD} y(1-y)\, s_C s_D s_1/s_2]\Big\}\end{aligned} \tag{13}$$

with $\chi_{\alpha\beta} = (z/2)(\epsilon_{\alpha\alpha} + \epsilon_{\beta\beta} - 2\epsilon_{\alpha\beta})/kT$ and with r_1 and r_2 given by eqs 10 and 11, respectively. Because χ_{SANS} in eq 13 is independent of blend composition, i.e., of ϕ_1 and ϕ_2, χ_{SANS} is identical with the effective χ parameter in the free energy of mixing for a binary A_xB_{1-x}/C_yD_{1-y} random copolymer blend. Ignoring the temperature-independent contribution to χ and taking each monomer to occupy a single lattice site, i.e., setting $s_A = s_B = s_C = s_D = 1$ in eq 13, reduce the latter equation to the well-known random copolymer FH expression derived by ten Brinke et al.[6]

$$\chi_{\rm FH} = \chi_{\rm AC}xy + \chi_{\rm BC}(1-x)y + \chi_{\rm AD}x(1-y) + \chi_{\rm BD}(1-x)(1-y) - \chi_{\rm AB}x(1-x) - \chi_{\rm CD}y(1-y) \quad (14)$$

Equation 14 is bilinear in x and y, while the temperature-dependent portion of eq 13 contains an additional dependence on x and y through the overall factor of $\sqrt{s_1 s_2}$ (as well as the more complicated dependence of the entropic portion of $\chi_{\rm SANS}$ on x and y).

The interaction parameter χ for a binary blend of two random copolymers of the same monomers species, say A_xB_{1-x} and A_yB_{1-y}, can be directly generated from eq 13 by replacing the subscripts C by A and D by B, respectively, to give

$$\chi_{\rm SANS} = \sqrt{s_1 s_2}\left\{\frac{1}{z^2}(r_1 - r_2)^2 + \chi_{\rm AB}(x-y)^2\left(\frac{s_{\rm A}s_{\rm B}}{s_1 s_2}\right)^2\right\} = \chi_{\rm s} + \chi_{\rm h} \quad (15)$$

with the individual chain average monomer site occupancies,

$$s_1 = s_{\rm A}x + s_{\rm B}(1-x) \quad \text{and} \quad s_2 = s_{\rm A}y + s_{\rm B}(1-y) \quad (16)$$

the partial entropic structure factors

$$r_1 \equiv \frac{N_2^{(1)}}{M_1} = \frac{[s_{\rm A} + s_{\rm A}^{(\rm tri)} + 3s_{\rm A}^{(\rm tetr)}]x + [s_{\rm B} + s_{\rm B}^{(\rm tri)} + 3s_{\rm B}^{(\rm tetr)}](1-x)}{s_{\rm A}x + s_{\rm B}(1-x)} \quad (17)$$

and

$$r_2 \equiv \frac{N_2^{(2)}}{M_2} = \frac{[s_{\rm A} + s_{\rm A}^{(\rm tri)} + 3s_{\rm A}^{(\rm tetr)}]y + [s_{\rm B} + s_{\rm B}^{(\rm tri)} + 3s_{\rm B}^{(\rm tetr)}](1-y)}{s_{\rm A}y + s_{\rm B}(1-y)} \quad (18)$$

and with the entropic and enthalpic contributions defined respectively as

$$\chi_{\rm s} = \sqrt{s_1 s_2}\,\frac{1}{z^2}\,(r_1 - r_2)^2$$

and

$$\chi_{\rm h} = \sqrt{s_1 s_2}\,\chi_{\rm AB}\,(x-y)^2\left(\frac{s_{\rm A}s_{\rm B}}{s_1 s_2}\right)^2$$

The well-known random copolymer FH form[6]

$$\chi_{\rm FH} = \chi_{\rm AB}\,(x-y)^2 \quad (19)$$

emerges from eq 14 in the single-site monomer limit of $s_{\rm A} = s_{\rm B} = 1$ and $s_{\rm A}^{(\rm tri)} = s_{\rm A}^{(\rm tetr)} = s_{\rm B}^{(\rm tri)} = s_{\rm B}^{(\rm tetr)} = 0$. The dependence on copolymer compositions x and y in eq 15 is much richer because of the entropic part and the factor of $(s_1s_2)^{-3/2}$ multiplying $\chi_{\rm AB}$.

When one blend species, say A, is a homopolymer and the second component, say C_yD_{1-y}, is a random copolymer, the corresponding expression for the $\chi_{\rm SANS}$ parameter likewise follows from eq 13 by introducing the substitutions B = A and $x = 1$, thereby leading to

$$\chi_{\rm SANS} = \sqrt{s_1 s_2}\left\{\frac{1}{z^2}(r_1 - r_2)^2 + \frac{1}{s_2}\left[\chi_{\rm AC}ys_{\rm C} + \chi_{\rm AD}(1-y)\,s_{\rm D} - \chi_{\rm CD}y\,(1-y)\,\frac{s_{\rm C}s_{\rm D}}{s_2}\right]\right\} \quad (20)$$

with $s_1 = s_{\rm A}$, $r_1 = (s_{\rm A} + s_{\rm A}^{(\rm tri)} + 3s_{\rm A}^{(\rm tetr)})/s_{\rm A}$, and s_2 and r_2 as given by eqs 16 and 18. Equation 20 is an extension of the well-known expression[7]

$$\chi_{\rm FH} = \chi_{\rm AC}y + \chi_{\rm AD}(1-y) - \chi_{\rm CD}y(1-y) \quad (21)$$

to A/C_yD_{1-y} systems with united atom structures for the A, C, and D monomers. The classic equations (14), (19), and (21) were derived assuming that the $\chi_{\alpha\beta}$ are of purely energetic origin, an assumption that is generally not valid.

III. Illustration of Computation of an Interaction Parameter

As a first illustration of the calculation of the $\chi_{\rm SANS}$ parameter for random copolymer systems, we consider the application of the theory to norbornene-*co*-ethylene (N_xE_{1-x}/N_yE_{1-y}) random copolymer blends. Elsewhere, the general theory of section II has been used to explain the observation by Delfolie and co-workers[1] that the miscibility of N_xE_{1-x}/N_yE_{1-y} binary blends improves significantly when both x and $y > 1/2$, an observation in sharp contrast to the predictions (eq 19) of random copolymer FH theory which implies that the blends are miscible when $|x - y|$ is less than a critical constant value c. The following describes in more detail the theory already used in the analysis of the data by Delfolie et al.[1]

Because of restrictions imposed by the geometry of a simple cubic lattice and the inability of the available theory to treat polymer chains containing cyclic (i.e., closed ring) units, the norbornene monomer has been modeled by an approximated structure (see Figure 1b) that has seven united atom groups and therefore occupies seven lattice sites ($s_{\rm N} = 7$). The ethylene monomer is represented by a two-bead dimer composed of two CH_2 groups that cover $s_{\rm E} = 2$ lattice sites. Thus, this simple model incorporates the actual monomer size disparity between these two types of monomers, a feature that influences the magnitude of the entropic component $\chi_{\rm s}$ of the interaction parameter $\chi_{\rm SANS}$, and it also affects the dependence of the enthalpic portion of $\chi_{\rm SANS}$ on composition (x and y). The individual chain average monomer site occupancy indices s_1 and s_2 of eq 16 are

$$s_1 = 7x + 2(1-x) \quad \text{and} \quad s_2 = 7y + 2(1-y) \quad (22)$$

where x and y denote the average compositions of random copolymer chains of species 1 and 2, respectively. Noticing that each norbornene monomer in Figure 1b involves three trifunctional united atom CH_n groups and that both norbornene and ethylene units have no tetrafunctional carbons, the partial entropic structure factors r_i of eqs 17 and 18 reduce to the compact forms

$$r_1 = \frac{(7+3)x + 2(1-x)}{7x + 2(1-x)} \quad (23)$$

and

$$r_2 = \frac{(7+3)y + 2(1-y)}{7y + 2(1-y)} \tag{24}$$

respectively. Thus, the entropic portion χ_s of χ_{SANS} equals

$$\chi_s = \sqrt{s_1 s_2}\,\frac{1}{z^2}(r_1 - r_2)^2 = \sqrt{(2+5x)\,(2+5y)}\,\frac{1}{z^2}\left[\frac{6(x-y)}{(2+5x)\,(2+5y)}\right]^2 \tag{25}$$

where the factor $\sqrt{s_1 s_2}$ again converts χ_s expressed per lattice site basis to χ_s per monomer basis.

The calculation of the enthalpic portion χ_h of χ_{SANS} is based on the extension of FH type counting to uncorrelated united atom group monomers. Consequently, we obtain

$$\chi_h = \sqrt{(2+5x)\,(2+5y)}[-\chi_{11}^{(h)} - \chi_{22}^{(h)} + 2\chi_{12}^{(h)}] \tag{26}$$

with the temperature-dependent portions $\chi_{ij}^{(h)}$ of χ_{ij} of eqs 4–6 given by

$$\chi_{11}^{(h)} = -\frac{z}{2}\left[\frac{\epsilon_{NN}}{kT}(m_N^{(1)})^2 + \frac{\epsilon_{EE}}{kT}(m_E^{(1)})^2 + 2\frac{\epsilon_{NE}}{kT}m_N^{(1)}\,m_E^{(1)}\right] \tag{27}$$

$$\chi_{22}^{(h)} = -\frac{z}{2}\left[\frac{\epsilon_{NN}}{kT}(m_N^{(2)})^2 + \frac{\epsilon_{EE}}{kT}(m_E^{(2)})^2 + 2\frac{\epsilon_{NE}}{kT}m_N^{(2)}\,m_E^{(2)}\right] \tag{28}$$

and

$$\chi_{12}^{(h)} = -\frac{z}{2}\left[\frac{\epsilon_{NN}}{kT}m_N^{(1)}\,m_N^{(2)} + \frac{\epsilon_{EE}}{kT}m_E^{(1)}\,m_E^{(2)} + \frac{\epsilon_{NE}}{kT}m_N^{(1)}\,m_E^{(2)} + \frac{\epsilon_{NE}}{kT}m_N^{(2)}\,m_E^{(1)}\right] \tag{29}$$

where ϵ_{NN}, ϵ_{EE}, and ϵ_{NE} designate monomer-averaged, nearest-neighbor van der Waals attractive energies between two norbornene, two ethylene, and norbornene–ethylene united atom groups, respectively, while the fractions $m_N^{(1)}$, $m_N^{(2)}$, $m_E^{(1)}$, and $m_E^{(2)}$ of the corresponding site occupancy indices s_1 and s_2 follow from eqs 7 and 8 as

$$m_N^{(1)} = 1 - m_E^{(1)} \equiv \frac{s_N x}{s_1} = \frac{7x}{7x + 2(1-x)} \tag{30}$$

and

$$m_N^{(2)} = 1 - m_E^{(1)} \equiv \frac{s_N y}{s_2} = \frac{7y}{7y + 2(1-y)} \tag{31}$$

respectively. Combining eqs 26–31 leads to the final form of χ_h as

$$\chi_h = \sqrt{(2+5x)(2+5y)}\,\frac{z}{2}\left[\frac{14(x-y)}{(2+5x)(2+5y)}\right]^2\frac{\epsilon}{kT} \tag{32}$$

where $\epsilon = \epsilon_{NN} + \epsilon_{EE} - 2\epsilon_{NE}$ is the exchange interaction energy and where the appearance of the square root factor reflects the customary definition of the χ parameters as representing monomer–monomer interactions.

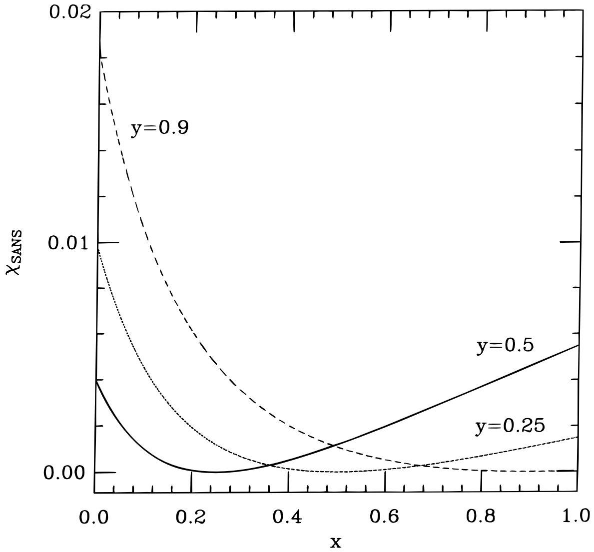

Figure 2. Computed interaction parameter χ_{SANS} for norbornene–ethylene random copolymer blends as a function of the composition x of component 1 (N_xE_{1-x}) for several compositions y of component 2 (N_yE_{1-y}). The exchange energy ϵ is taken as $\epsilon/kT = 1 \times 10^{-4}$. Reference 1 provides additional examples along with illustration of the influence of chain flexibility.

The total interaction parameter χ_{SANS} is a sum of the entropic and enthalpic contributions,

$$\chi_{SANS} = \chi_s + \chi_h = \sqrt{(2+5x)\,(2+5y)} \times \left[\frac{x-y}{(2+5x)\,(2+5y)}\right]^2\left[\frac{36}{z^2} + \frac{z}{2}\,196\,\frac{\epsilon}{kT}\right] \tag{33}$$

Figure 2 depicts the computed χ_{SANS} of eq 33 as a function of the random copolymer 1 composition x for several values of the random copolymer 2 composition y. When both x and y are large, χ_{SANS} indeed becomes small, suggesting a better miscibility of N_xE_{1-x} and N_yE_{1-y} random copolymers, in accord with the experimental observation of Delfolie et al.[1]

Equations 15 and 33 have been derived assuming that all bonds in the random copolymer chains are completely flexible. In order to test this asumption, we have also studied how stiffness in the norbornene side group, as well as the stiffness of the bond connecting two sequential norbornene units, affects the interaction parameter χ_{SANS} and the blend miscibilities. As described in refs 11 and 35, chain semiflexibility influences the partial entropic structural parameters r_i. The rigidity of the actual norbornene monomers is introduced into our model by taking the two pairs of side group bonds (see Figure 1b) as completely rigid. r_i for an A_xB_{1-x} random copolymer chain with $n_{2,stiff}^{(A)}$ and $n_{2,stiff}^{(B)}$ stiff pairs of bonds in monomers of species A and B, respectively, is given by the general formula

$$r_i = \{[s_A + s_A^{(tri)} + 3s_A^{(tetr)} - n_{2,stiff}^{(A)}]x + [s_B + s_B^{(tri)} + 3s_B^{(tetr)} - n_{2,stiff}^{(B)}](1-x)\}/ s_A x + s_B(1-x) \tag{34}$$

Thus, specializing eq 34 to N_xE_{1-x}/N_yE_{1-y} blends and setting $n_{2,stiff}^{(N)} = 2$ and $n_{2,stiff}^{(E)} = 0$ give

$$r_1 = \frac{(7 + 3 - 2)x + 2(1 - x)}{7x + 2(1 - x)} \qquad (35)$$

$$r_2 = \frac{(7 + 3 - 2)y + 2(1 - y)}{7y + 2(1 - y)} \qquad (36)$$

and the entropic portion of the monomer−monomer interaction parameter becomes

$$\chi_s = \sqrt{s_1 s_2}\,\frac{1}{z^2}(r_1 - r_2)^2 = \sqrt{(2 + 5x)(2 + 5y)}\,\frac{1}{z^2}\left[\frac{2(x - y)}{(2 + 5x)(2 + 5y)}\right]^2 \qquad (37)$$

Comparing eqs 37 and 25 indicates that the rigidity of norbornene monomers leads to a smaller entropic portion χ_s of χ_{SANS} and ultimately to an improved miscibility of norbornene−ethylene random copolymers. The ethalpic portion χ_h of χ_{SANS} remains unchanged within this particular united atom model extenstion of FH theory which neglects all correlations arising from chain connectivity.

While the presence of rigid bonds inside norbornene side groups reflects the stiffness of the actual norbornene ring, the strong steric interactions between bonded norbornene units may be modeled by treating bonds connecting adjacent norbornene monomers as semiflexible. The structural entropic parameter r_i for the A_xB_{1-x} random copolymer chains with the average number n_{AA} of bonds (taken as semiflexible) between monomers of species A emerges from LCT as

$$r_i = [s_A + s_A^{(tri)} + 3s_A^{(tetr)}]x + [s_B + s_B^{(tri)} + 3s_B^{(tetr)}] \times (1 - x) + 2(g - 1)n_{AA}/(n_A + n_B)\Big/ s_A x + s_B(1 - x) \qquad (38)$$

where $g = z/[z - 1 + \exp(E_b/k_BT)]$ and E_b is the trans−gauche energy difference. Note that the quantity n_{AA} is a sequence-dependent quantity because, for example, $n_{AA} = 0$ for a perfectly alternating $(AB)_n$ copolymer, while, at the opposite limit of an A_nB_m diblock copolymer, we have $n_{AA} = n_A - 1$. The specialization of eq 38 to N_xE_{1-x}/N_yE_{1-y} blends yields

$$r_1 \simeq \frac{(7 + 3)x + 2(1 - x) + 2(g - 1)x^2}{7x + 2(1 - x)} \qquad (39)$$

$$r_2 \simeq \frac{(7 + 3)y + 2(1 - y) + 2(g - 1)y^2}{7y + 2(1 - y)} \qquad (40)$$

and the final entropic χ_s is

$$\chi_s = \sqrt{s_1 s_2}\,\frac{1}{z^2}(r_1 - r_2)^2 = \sqrt{(2 + 5x)(2 + 5y)}\,\frac{1}{z^2} \times \left[\frac{6(x - y) + 2(g - 1)\,[10xy(x - y) + 2(x^2 - y^2)]}{(2 + 5x)(2 + 5y)}\right]^2 \qquad (41)$$

Again, the enthalpic portion χ_h is unchanged and is given by eq 32. Because the trans−gauche energy difference E_b satisfies the condition $E_b \geq 0$ and because the stiffness factor g meets the restriction $g \leq 1$, a simple analysis of eqs 41 and 25 suggests that the semiflexibility of bonds connecting norbornene monomers likewise renders the norbornene−ethylene blends more miscible. Another possible model assumes both the semiflexibility of backbone bonds and the rigidity of norbornene side groups, leading to to a slight modification of eq 41,

$$\chi_s = \sqrt{s_1 s_2}\,\frac{1}{z^2}(r_1 - r_2)^2 = \sqrt{(2 + 5x)(2 + 5y)}\,\frac{1}{z^2} \times \left[\frac{2(x - y) + 2(g - 1)\,[10xy(x - y) + 2(x^2 - y^2)]}{(2 + 5x)(2 + 5y)}\right]^2 \qquad (42)$$

These models are compared elsewhere with experimental data,[1] and the entropic χ_s is found to exert a dominant role in influencing the miscibilities of the norbornene−ethylene blends.

IV. Isotopic Mixtures of sPB

The simplest random copolymer blends are represented by A_xB_{1-x}/A_yB_{1-y} mixtures which contain only a pair of different monomers, and therefore a minimum number of microscopic van der Waals energies $\{\epsilon_{\alpha\beta}\}$ is required to describe the polymer−polymer interactions in these systems. Thus, analyzing experimental data for these mixtures over a range of copolymer compositions (x, y) and blend compositions (ϕ_1, ϕ_2) would appear to provide the simplest tests of the theory. Perhaps, the most widely studied A_xB_{1-x}/A_yB_{1-y} blends are those obtained from saturated poly(butadiene) (sPB) polymers. Both blend components are random copolymers because of the presence of varying degrees of 1,2 and 1,4 units. The sPB systems have been extensively investigated by Graessley[21] and Klein[28] and their respective co-workers using the SANS method and a nuclear reaction analysis, respectively. Both groups employ the same samples in which the A_xB_{1-x} copolymers are hydrogenated sPB chains, whereas the A_yB_{1-y} component is a *partially deuterated* sPB. Scheffold et al. demonstrate[28] the general quantitative agreement in the overall values of χ between these two very different measurements, but some systematic departures do appear. In particular, fits of the two sets of data to the form $\chi = \chi_s + \chi_h'/T$ yield rather different χ_s and χ_h' as shown in Table 1 for the three binary blends treated by both methods. While the temperature-independent portion χ_s of χ, as determined by Scheffold et al., is generally rather small (on the order of 10^{-5}) with both positive and negative signs, the values of χ_s extracted from the SANS experiments are always negative and large ($-10^{-3} < \chi_s < -10^{-4}$). Also, there are significant differences (up to 250%) in the temperature dependence of the χ parameter (i.e., in the coefficients χ_h') extracted from these two methods. These disparities in χ_s and in χ_h' between the two data sets (see Table 1) represent one source of uncertainty, and we should not seek to obtain better agreement between theory and experiment than provided by this uncertainty and/or the stated experimental errors. Another possible source of uncertainty arises from the method of preparation of the samples. In order to have matched pairs of hydrogenated and deuterated sPB chains for the determination of radii of gyration, etc., the same unsaturated perhydro-PB samples are then either hydrogenated or deuterated. Unfortunately, the deuteration is not simple, and a certain degree of H/D scrambling occurs. Thus, the deuterium content varies in an unknown fashion among monomers of a single chain and also within the united atom CH_n groups of each monomer. Because the current viewpoint ascribes the details of the SANS scattering

Table 1. Comparison between Small-Angle Neutron Scattering (SANS) Interaction Parameter $\chi_{SANS} = \chi_s + \chi_h'/T$ of Saturated Poly(butadiene) Blends As Obtained for Identical Samples by Different Experimental Methods

	H52/D66 ($\phi_H = 0.797$)		H66/D52 ($\phi_H = 0.486$)		H88/D78 ($\phi_H = 0.501$)	
	$\chi_s \times 10^4$	χ_h'	$\chi_s \times 10^4$	χ_h'	$\chi_s \times 10^4$	χ_h'
Graessley et al.[21]	−13.6	1.12	−6.57	0.656	−8.17	0.732
Scheffold et al.[28]	4.56	0.428	−1.22	0.458	-9.28×10^{-3}	0.469

to the influence of H/D differences on the interaction energies $\epsilon_{\alpha\beta}$, the random partial deuterium substitution leads to an additional interaction randomness that is presently not amenable to modeling with the theory developed here. (The random partial deuteration presumably likewise affects the nuclear reaction analysis experiments.)

The theory of section II is applied separately to the data from both types of experiments by fitting the interaction parameters to data for a number of distinct binary blends. We begin with the SANS data of Graessley et al.[21] where the agreement between theory and experiment is not as good as that for the nuclear reaction analysis data of Scheffold et al.[28] Let component 1 designate an A_xB_{1-x} random copolymer with a fraction x of hydrogenated 1,2 units and a fraction $1 - x$ of hydrogenated 1,4 units ($A \equiv$ H1,2 and $B \equiv$ H1,4), whereas component 2 denotes a statistical copolymer C_yD_{1-y} of partially deuterated 1,2 and 1,4 PB monomers ($C \equiv$ D1,2 and $D \equiv$ D1,4). Figure 1a depicts united atom monomer structures for both 1,2 and 1,4 monomers. The isotopic sPB blends are now treated formally as A_xB_{1-x}/C_yD_{1-y} mixtures, but further assumptions (see below) enable us to describe them in terms of three energy parameters, i.e., on a level comparable to that for A_xB_{1-x}/A_yB_{1-y} blends. Noticing from Figure 1b that the monomer structures for sPB imply that $s_A = s_B = s_C = s_D = 4$, $s_A^{(tri)} = s_C^{(tri)} = 1$, $s_B^{(tri)} = s_D^{(tri)} = 0$, and $s_A^{(tetr)} = s_B^{(tetr)} = s_C^{(tetr)} = s_D^{(tetr)} = 0$, the partial entropic structural parameters r_1 and r_2 of eqs 10 and 11 simplify to

$$r_1 = \frac{(4+1)x + 4(1-x)}{4x + 4(1-x)} = \frac{x+4}{4} \tag{43}$$

and

$$r_2 = \frac{(4+1)y + 4(1-y)}{4y + 4(1-y)} = \frac{y+4}{4} \tag{44}$$

while the average monomer site occupancy indices s_1 and s_2 of eqs 16 are $s_1 = 4x + 4(1 - x) = 4$ and $s_2 = 4y + 4(1 - y) = 4$. Our analysis of the experimental SANS data[21] for isotopic sPB blends is based on eq 13 and on two further simplifying assumptions that are designed to reduce the number of adjustable parameters to the bare minimum. First, all heterocontact interaction energies $\epsilon_{\alpha\beta}$ ($\beta \neq \alpha$) are assumed to satisfy the Berthelot combining rule,[29] i.e.,

$$\epsilon_{\alpha\beta} = (\epsilon_{\alpha\alpha}\epsilon_{\beta\beta})^{1/2}, \quad \alpha, \beta = \mathrm{A, B, C, D}, \quad \beta \neq \alpha \tag{45}$$

The second assumption invokes the polarizability model of Bates et al.,[30] which postulates a simple scaling relation between the interaction energies for two hydrogenated and two deuterated monomer groups

$$\epsilon_{CC} = \gamma^2\epsilon_{AA}, \quad \gamma < 1 \tag{46}$$

$$\epsilon_{DD} = \gamma^2\epsilon_{BB}, \quad \gamma < 1 \tag{47}$$

where the scaling factor γ is less than unity to represent the weaker homocontact attraction of the partially deuterated species. Again, to minimize the number of parameters, γ is taken as the same for 1,2 and 1,4 units. This assumption also ignores the fact that the experimental samples have varying degrees of partial deuteration and should therefore be described using factors γ and scattering lengths that vary with the monomers' deuterium content. As already mentioned, this variable deuteration, therefore, somewhat limits the theoretical analysis of the experimental data.

Given the above model and assumptions, the small-angle neutron scattering χ_{SANS} parameter of eq 13 is converted to the rather compact result

$$\chi_{SANS} = \frac{2z}{kT}\{(1-\gamma)[y\sqrt{\epsilon_{AA}} + (1-y)\sqrt{\epsilon_{BB}}] + (x-y)(\sqrt{\epsilon_{AA}} - \sqrt{\epsilon_{BB}})\}^2 + \frac{1}{4z^2}[x-y]^2 \tag{48}$$

The expression for χ_{SANS} in eq 48 contains only three adjustable parameters: two self-interaction van der Waals energies ϵ_{AA} and ϵ_{BB} for the 1,2 and 1,4 perhydrogenated species, respectively, and the polarizability scaling factor γ. The first term in braces in eq 48 dominates over the second, but the hydrogen/deuterium swap effect is lost without this second term, a feature consistent with the nature of the swap phenomenon which arises from "small" differences between the two isotopic species. Note that both the entropic and energetic portions of χ_{SANS} from eq 48 individually exhibit structures similar to the form

$$\chi_\delta = \frac{v_0}{2kT}[\delta_1 - \delta_2]^2 \tag{49}$$

that emerges from regular solution theory and that has been used by Graessley, Lohse, et al.[15,17,18,21,31] to describe their experimental data for χ_{SANS} in terms of the pure-component solubility parameters δ_1 and δ_2. The lack of a separate entropic portion in solubility parameter theory is thus exhibited by the application of LCT to the norbornene-*co*-ethylene blends as a serious flaw in solubility parameter theory, although empirical analysis used to interpret data may incorporate entropic contributions to χ_{SANS}. An improved solubility parameter theory might be formulated by using eq 49 *only* for χ_h (as is theoretically justified) and a separate expression for $\chi_s \propto (r_1 - r_2)^2$ as in LCT. An analysis of this approach is left for future work.

The three parameters in eq 48 are fit to experimental data[21] for $\chi_{SANS}(T)$ from a series of 10 isotopic sPB random copolymer blends with varying compositions $x \neq y$. The comparison of theory and experiment is illustrated in Figure 3a for a pair of systems that are denoted as H38/D25 and H25/D38, following the notation employed by Graessley et al.[21] where, for instance, H38/D25 corresponds to the blend $A_{0.38}B_{0.62}/C_{0.25}D_{0.75}$; i.e., the numbers reflect the percentage of 1,2 units in the copolymers. The experimental points are designated

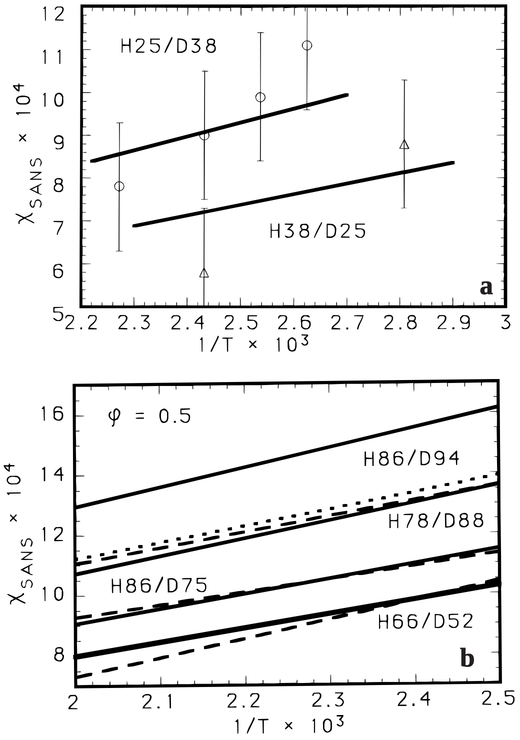

Figure 3. (a) Interaction parameter $\chi_{SANS}(T)$ as a function of inverse temperature $1/T$ for symmetric ($\phi_1 = \phi_2 = 0.5$) H25/D38 and H38/D25 isotopic saturated poly(butadiene) blends. Solid lines are the LCT fits to the experimental data[21] for 10 HxDy and HyDx mixtures ($y > x$). Circles and triangles denote data for the H25/D38 and H38/D25 mixtures, respectively. The experimental error bars for χ_{SANS} are taken as $\pm 1.5 \times 10^{-4}$ as the stated upper limits (see footnote *a* on p 2576 in ref 21). The values of the adjustable parameters ϵ_{AA}, ϵ_{BB}, and γ are specified in the text. (b) Interaction parameter $\chi_{SANS}(T)$ as a function of inverse temperature $1/T$ for symmetric ($\phi_1 = \phi_2 = 0.5$) H66/D52, H86/D75, H78/D88, and H86/D94 isotopic saturated poly(butadiene) blends. Solid lines are the LCT fits to the experimental data by Scheffold et al.[28] for eight HxDy and HyDx mixtures ($y > x$). The experimental data for the four mixtures are denoted by dashed and dotted lines. The values of the adjustable parameters are $\epsilon_{AA} = 247.01$ K, $\epsilon_{BB} = 249.09$ K, $\epsilon_{AB} = 248.35$ K, and $\gamma = 0.9864$.

by circles and triangles, and the lines present the theoretical fits of eq 48 to experimental data[21] for 10 distinct binary blends. The experimental error bars are taken as $\pm 1.5 \times 10^{-4}$, as given by Graessley et al.,[21] who note that the experimental uncertainty is somewhat less when comparing χ_{SANS} for a single blend at different temperatures. The interaction energies ϵ_{AA} and ϵ_{BB} and the polarizability factor γ are obtained as $\epsilon_{AA} \equiv \epsilon_{1,2-1,2} = 238.30$ K, $\epsilon_{BB} \equiv \epsilon_{1,4-1,4} = 240.79$ K, and $\gamma = 0.9901$, with a standard deviation of $\pm 1.7 \times 10^{-4}$ which is comparable to the experimental error bars. The value of γ is in line with the polarizability model of Bates et al.[30] for the interactions of CH_n and CD_n groups ($\alpha_{C-D}/\alpha_{C-H} = 0.98-0.99$). The fits are not, however, unique, and there are many sets of ϵ_{AA}, ϵ_{BB}, and γ that yield standard deviation similar to and accuracies comparable to those in Figure 3a.

An important feature of eq 48 is the proper description of the deuterium swap effect. A larger χ is always obtained from this equation when the more branched polyolefin component is deuterated. The same behavior appears in numerous experiments[21,28,32−34] and follows directly from eq 48 provided that $\epsilon_{BB} > \epsilon_{AA}$. The present finding that the interaction energy $\epsilon_{\alpha\alpha}$ is higher for the less branched polyolefin species α is also consistent with our previous fits[35] of LCT to equation of state (*PVT*) data for polyolefin melts as well as with the analysis[36−38] of Schweizer and co-workers.

Table 2. Comparison of Small-Angle Neutron Scattering (SANS) Interaction Parameter $\chi_{SANS} = \chi_s + \chi'_h/T$ of Saturated Poly(butadiene) Blends As Determined from the Nuclear Reaction Analysis Experiments[28] and from the LCT Fit to the Nuclear Reaction Data

	$\chi_s \times 10^{-4}$		χ'_h	
blend ($\phi_H = 0.5$)	experiment	theory	experiment	theory
H52/D66	3.87	1.36	0.363	0.462
H66/D52	−1.20	1.36	0.459	0.363
H66/D75	0.27	0.56	0.410	0.526
H75/D86	0.80	0.84	0.543	0.508
H78/D88	−0.95	0.69	0.583	0.518
H86/D75	−0.70	0.84	0.488	0.421
H86/D94	0	0.25	0.647	0.548
H88/D78	−0.009	0.69	0.469	0.431

Figure 3a demonstrates that the theory reproduces the overall values of the χ parameter within the stated experimetal error bars. Note that we employ only three parameters to describe all of the binary sPB blends, while Graessley et al. describe each of the 10 individual sPB pure-component systems with separate sets of temperature-dependent solubility parameters (23 total solubility parameters in all).[31] However, despite this huge contraction of the data into just three parameters, the slopes χ'_h of $\chi_{SANS}(1/T)$ vs $1/T$ differ considerably between the simple extended theory and experiment. Some improvements in the theoretical χ'_h are possible by introducing blend compressibility, different chain stiffness for the two blend components, or by allowing γ to differ slightly for the 1,2 and 1,4 units, but given the experimental error bars (and the comparisons below), it is not worth describing these minor improvements at this juncture. Lifting the Berthelot approximation of eq 45 (i.e., treating heterocontact interaction energy ϵ_{AB} as an additional adjustable parameter) does not produce a better fit.

One feature contributing to the differences between the experimental and theoretical slopes in Figure 3a is the presence of a rather huge negative temperature-independent portion χ_s of χ_{SANS} for all of the binary isotopic sPB blends studied by Graessley et al.[21] (for instance, $\chi_s = -0.0035$ and -0.0022 for the H08/D25 and H25/D08 blends, respectively, and see Table 1). In contrast, the entropic part χ_s of χ_{SANS} in eq 48 is always positive

$$\chi_s = \sqrt{s_1 s_2}\,\frac{1}{z^2}(r_1 - r_2)^2 = \frac{1}{4z^2}(x - y)^2 \qquad (50)$$

while the inclusion of compressibility and chain semiflexibility can render χ_s slightly negative for high molecular weight blends. On the other hand, both the entropic and enthalpic portions of χ_{SANS} are quite different between the data of Graessley et al. and the data of Scheffold et al. (see Table 1). Because the individual overall χ parameters determined from these two experimental methods agree to within the mutual error bars (assuming that those corresponding to the data of Scheffold et al. are on the order of $\pm 1.5 \times 10^{-4}$), it is relevant to compare LCT also with the neutron reaction analysis experiments.

Figure 3b presents several examples of our fits to the data of Klein and co-workers for eight binary sPB blends. The fits (see also Table 2) are reasonable, with the discrepancies in χ'_h not exceeding 30%. Apart from the H52/D66 sample, the experimental χ_s are all quite small and presumably less than experimental error bars. The superior agreement of the theoretical $\{\chi'_h\}$ with the $\{\chi'_h\}$ from the nuclear reaction analysis data than with the $\{\chi'_h\}$ from the SANS data of Graessley et al. is as anticipated because the entropic portions χ_s of χ_{SANS}, determined by Scheffold et al., are generally comparable in magnitude to the theoretical predictions of eq 48. The fit quality improves noticably when the heterocontact interaction energy departs from the Berthelot rule and is treated as an extra adjustable parameter. Table 2 and the examples in Figure 3b are generated using a non-Berthelot correction $\epsilon_{AB} = \sqrt{\epsilon_{AA}\epsilon_{BB}}(1 + \lambda)$ and the parameter set $\epsilon_{AA} = 247.01$ K, $\epsilon_{BB} = 249.09$ K, $\epsilon_{AB} = 248.35$ K (i.e., $\lambda = 1.2 \times 10^{-3}$), and $\gamma = 0.9864$. These four adjustable parameters vary (but only slightly) from the values obtained by fitting eq 48 to the data of Graessley et al. ($\epsilon_{AA} = 238.30$ K, $\epsilon_{BB} = 240.79$ K, $\epsilon_{AB} = 239.54$ K, and $\gamma = 0.9901$).

V. Miscibility Trends in Random Copolymer Blends of Different Polyolefins

Our previous papers[11,19,23,39] demonstrate how general qualitative trends in miscibility of weakly interacting systems, such as polyolefin blends, can be inferred simply by inspecting the relative magnitudes of the blend entropic structural parameter r

$$r \equiv |r_1 - r_2| \tag{51}$$

The LCT derives[14,23] the entropic parameter r as a measure of the structural asymmetry between the two blend species and as completely determined by the interaction parameter χ_{SANS} in the incompressible, high molecular weight, athermal, fully flexible chain limit. The theory indicates that a smaller r corresponds to a smaller χ_s and to better miscibility if the interaction energies $\epsilon_{\alpha\beta}$ are similar enough, i.e., if $\chi_s = \sqrt{s_1 s_2}(r/z)^2$ is a good approximation to the overall χ_{SANS}. Our recent work[19] shows, for instance, that the quantity r correlates well with the observed miscibilities of binary blends of poly(propylene) and hydrogenated poly(butadiene) with varying degrees of 1,2 and 1,4 units. Here we illustrate further the utility of this simple correlation for binary polyolefin blends formed by a pair of random copolymers.

The blends analyzed below have as a common component a hydrogenated poly(butadiene) with 97% of 1,2 units. The other component (called component 1) is a random copolymer of either poly(propylene) (PP) and poly(ethylene) (PE), of poly(butene-1) (PB1) and PE, of poly(hexene-1) (PH1) and PE, or of poly(octene-1) (PO1) and PE. Figure 1c depicts the united atom structures for the PE, PP, PB1, PH1, and PO1 monomers. The SANS interaction parameters χ_{SANS} for these blends (labeled as PP_xPE_{1-x}/H97, $PB1_xPE_{1-x}$/H97, $PH1_xPE1-x$/H97, and $PO1_xPE_{1-x}$/H97) have been converted by Reichart et al.[40] into a set of solubility parameters $\delta_{blend} = (\delta_1 - \delta_{H97})$ as a function of composition x, where $\chi_{exp} \propto \delta_{blend}{}^2$ and where eq 49 is used in their analysis with temperature-dependent factors v_0 that are not given in ref 40 to enable the conversion of δ_{blend} to χ_{SANS}. Thus, we focus on a comparison of general trends for $|r_1 - r_{H97}|$ and δ_{blend}. All binary blends display the same composition dependence: as x grows, $\delta_{blend}(T)$ and, therefore, $\chi_{SANS}^{exp}(T) = const\ \delta_{blend}(T)^2$ both decrease, thereby indicating improved blend miscibility with an increase in the percentage of the more branched monomer species in the variable random copolymer (component 1).

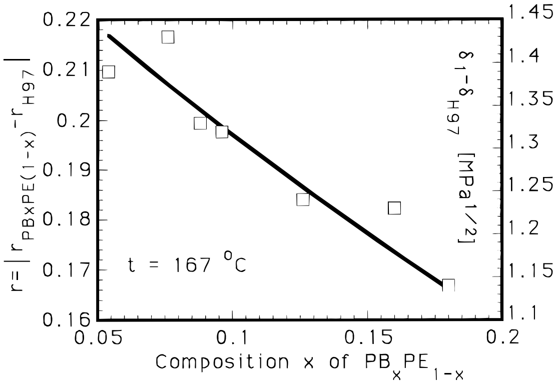

Figure 4. Comparison of the structural parameter r (solid line) and the solubility parameter $\delta_{blend} = (\delta_1 - \delta_{H97})$ data[40] (squares) for $PB1_xPE_{1-x}$/H97 blends as common measures of blend miscibility. Both r and $\delta_1 - \delta_{H97}$ are plotted using separate scales as functions of the composition x of the $PB1_xPE_{1-x}$ component.

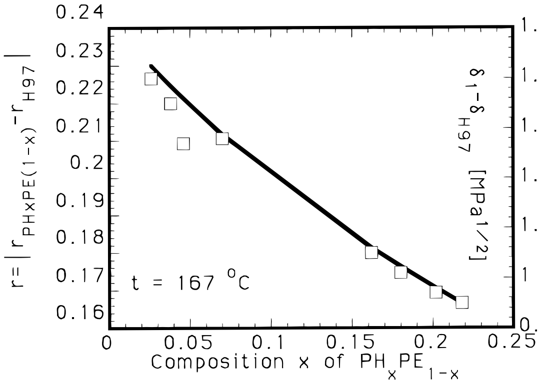

Figure 5. Same as Figure 4 but for $PH1_xPE_{1-x}$/H97 blends.

The same trend can be derived from the composition dependence of the blend entropic parameter r

$$r = |r_1 - r_{H97}| \tag{52}$$

where the partial entropic structural parameters r_i are readily obtained from eqs 8 and 9 as functions of the random copolymer compositions

$$r_{PP_xPE_{1-x}} = \frac{(3+1)x + 2(1-x)}{3x + 2(1-x)} = \frac{2+2x}{2+x} \tag{53}$$

$$r_{PB1_xPE_{1-x}} = \frac{(4+1)x + 2(1-x)}{4x + 2(1-x)} = \frac{2+3x}{2+2x} \tag{54}$$

$$r_{PH1_xPE_{1-x}} = \frac{(6+1)x + 2(1-x)}{6x + 2(1-x)} = \frac{2+5x}{2+4x} \tag{55}$$

$$r_{PO1_xPE_{1-x}} = \frac{(8+1)x + 2(1-x)}{8x + 2(1-x)} = \frac{2+7x}{2+6x} \tag{56}$$

$$r_{H97} = \frac{(4+1)(0.97) + 4(0.003)}{4(0.97) + 4(0.03)} = 1.2425 \tag{57}$$

Figures 4 and 5 compare the variation of r and δ_{blend} with the copolymer composition x for the $PB1_xPE_{1-x}$/

H97 and PH1$_x$PE$_{1-x}$/H97 blends, respectively. The solid line illustrates the computed $r = r(x)$ curve, while squares represent experimental data[40] for δ_{blend} at $t = 167$ °C. The different units for r and δ_{blend} require the use of plots with two separate ordinates. Similar agreement between the composition dependence of $r(x)$ and that of $\delta_{\text{blend}}(x)$ [and thus that of $\chi_{\text{SANS}}^{\text{exp}}(x)$] is found for PP$_xPE_{1-x}$/H97 and PO1$_xPE_{1-x}$/H97 blends. Hence, the entropic structural parameter again provides a very simple first guide to relative miscibilities as a function of random copolymer composition for blends containing chemically rather similar monomers.

VI. Discussion

Our extension of random copolymer FH theory is based on two improvements: describing the polymer−polymer interactions in terms of the interactions between united atom groups and completely determining (with no adjustable parameters) the temperature-independent portion χ_s of the interaction parameter χ from the monomer structures (see Figure 1) and the incompressible, athermal, fully flexible, long-chain limit of LCT. Beyond the obvious advantages of a more realistic microscopic molecular basis, the benefits of this new theoretical approach lie in its simple, tractable, analytical nature and in the presence of no extra adjustable parameters beyond those already employed in standard random copolymer FH theory. The calculation of the entropic component of χ_{SANS} follows from the elementary counting of the numbers of tri- and tetrafunctional united atom groups in the individual monomer structures such as those illustrated in Figure 1. Likewise, the contact probabilities, which describe the temperature-dependent part of χ, are completely determined by the van der Waals attractive interaction energies $\{\epsilon_{\alpha\beta}\}$ between united atom groups, by the numbers of united atom groups in the monomer structures, and by the copolymer compositions x and y. This improved random copolymer FH theory has been successfully applied by Delfolie et al.[1] to explain the main features of the miscibility diagram for norbornene−ethylene random copolymer blends that contrast sharply with the predictions of random copolymer FH theory. Section III applies the theory to this particular system in order to illustrate the implementation of the theory and thereby to provide guidance for its future use.

In addition to treating norbornene−ethylene random copolymers as fully flexible chains, we also discuss briefly how chain semiflexibility (as well as the rigidity of norbornene side groups) influences the effective interaction parameter and the blend miscibility. The modeling of rigid norbornene side groups is accomplished without introducing additional parameters, while other models of chain semiflexibility contain extra parameters corresponding to conformational energy differences. One of the models introduces chain semiflexibility due to steric interactions between bonded norbornene units, a model which accounts for a sequence dependence to χ in a microscopically transparent fashion. A similar type of model may be used to describe the dependence of melt, blend, etc., properties on tacticity by accounting for the microscopic influence of tacticity on the local chain semiflexibility. Because these semiflexible chain models require the introduction of additional ("trans−gauche") conformational energies as well as an extension of the counting methods for χ_s, a more detailed study of the semiflexibility is deferred to a future work. Nevertheless, the models discussed serve to illustrate some basic features of the theory as applied to semiflexible polymers.

Comparisons with experimental SANS data for isotopic saturated poly(butadiene) blends yield general agreement with our simplified theory which also correctly predicts the deuterium swap effect. The reduction of the χ_{SANS} data for 10 binary blends of random copolymers of saturated poly(butadienes) down to three parameters represents the success of the simple, easily used theory. A similar comparison with experimental data from a nuclear reaction analysis employs an additional parameter and provides quite good agreement because the computed slopes χ_h' of χ_{SANS} vs $1/T$ are much more similar to the experimental values of χ_h' for this data set. A more stringent test of the theory requires experimental data with greatly reduced error bars. Data of this type might be generated by experiments in which one of the saturated poly(butadienes) is fully deuterated and the other is fully protonated because this system would yield better scattering contrast, reducing experimental errors. Moreover, the description of this system would be more consistent with employing a single deuteration factor γ for all deuterated chains. A deeper understanding of the subtle microscopic features governing the miscibility of random copolymer blends may ultimately require (and guide) the development of more elaborate theory. An improved theory might contain correlation corrections to the contact probabilities in the energetic portions of χ_{ij}, corrections that quantify and extend the vague Guggenheim surface fraction concept[41,42] to random copolymer chains with structured monomers and chain semiflexibility. In addition, it will ultimately become necessary to drop the assumption of monomer-averaged interactions because off-lattice simulations of alkanes indicate rather different energy parameters for the CH_3-CH_3, CH_2-CH_2, and $CH-CH$ interactions. Unfortunately, the greater microscopic realism of such descriptions must come with diminished analytical tractability.

Acknowledgment. This research is supported, in part, by Grant DAAG55-97-1-0162 from ARO. We are grateful to a reviewer for helpful suggestions concerning the data analysis.

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MA991747G