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Lattice Cluster Theory for Copolymer Blends: General Theory in the Incompressible System, Long Chain Limit*

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The lattice cluster theory is developed for binary blends of two structured monomer copolymers in the simplifying limit of an incompressible system and high molecular weights. The major advance in the present theory is the inclusion of nonrandom mixing effects that lead to a monomer sequence dependence of the Helmholtz free energy without the introduction of new adjustable parameters beyond those present in descriptions of binary homopolymer blends formed from the constituent monomers. Equivalently, the sequence dependent contributions are shown to emerge from a proper determination of the "surface fractions" in individual copolymer chains. The general theory applies to blends of random copolymer, diblock copolymers, alternating copolymers, as well as of copolymers with kinetically controlled monomer sequences. The theory is illustrated for purely random copolymer blends of deuterated and hydrogenated polybutadienes, where the computed phase boundaries depart qualitatively from those predicted by random copolymer Flory-Huggins theory.

Key words: lattice model, polymers, isotope effect, mixtures, miscibility

The technological and scientific importance of random copolymers arises, in part, from their ability to enhance the mixing of otherwise immiscible systems. The earliest theories [1–7] of random copolymer systems apply Flory-Huggins type theory to random copolymers. This random copolymer extension [2,3] of Flory-Huggins theory is widely used, in part, because of its simplicity but also because it captures several important physical trends. The fact that these earliest theories [1–7] are enormously useful in explaining the general patterns of miscibility observed in many random copolymer containing systems cannot, however, overshadow many limitations of the underlying classic FH theory. These limitations include the complete insensitivity of the predicted thermodynamic properties to the monomer sequence, to chain architectures, and to individual monomer structures. As a partial remedy for these deficiencies, some theoretical descriptions [8–10] postulate an explicit dependence of the system's free energy on the monomer sequence by introducing a set of phenomenological interaction parameters $\chi_{ijk,lmn}$ between triads of sequential monomers on two different polymer chains and by employing additional *ad hoc* assumptions to re-

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*Dedicated to Prof. Jan Stecki on the occasion of his 70th birthday.

duce the huge number of resulting $\chi_{ijk,lmn}$ parameters to a manageable few additional adjustable parameters beyond those in random copolymer FH theory.

We have developed the lattice cluster theory [11–14], which overcomes all the above mentioned deficiencies of FH theory. By combining a significantly more advanced solution to the lattice model of polymer systems with a description of monomer molecular structures, the LCT free energy emerges naturally as monomer sequence dependent without the need for additional adjustable parameters beyond those necessary for treating binary blends of homopolymers constituted from the monomers present in the copolymer chains [14]. The LCT achieves this improved description, in part, by use of a cluster expansion to include contributions from nonrandom mixing effects, *i.e.*, from short range correlations neglected entirely by FH theory. Indeed, the lowest order LCT for copolymers is equivalent to a compressible system extension of random copolymer FH theory, in which the interactions are described more realistically as arising between submonomer units, called united atom groups, that are used to represent the monomer molecular structures [14].

The derivation of this more molecularly oriented LCT description of copolymer systems, however, involves enormous algebraic complexity, especially when the system is treated as compressible (necessity for describing the pressure dependence) and when the individual monomers of both random copolymers are permitted to have arbitrarily chosen molecular structures [14]. This complexity stems from the need for averaging the nonrandom mixing corrections to the free energy over all possible specific monomer sequences for all chains in the system. Because of this technical complexity, the extension of the LCT for compressible binary mixtures of statistical copolymers has so far been accomplished [14,15] for a very limited number of special cases.

In addition to developing complete and comprehensive theories, there is also a need for more approximate, analytically simpler, yet still more realistic theories with a minimal number of adjustable parameters. For example, we have recently developed [16] a simplified version of the LCT for statistical copolymers that represents an extension of random copolymer FH theory [2,3]. This more approximate theory, called the random copolymer lattice cluster theory for pedestrians, is analytically quite simple and is designed for probing general physical trends that lie outside the scope of random copolymer FH theory. Like FH theory, this simplified theoretical approach [16] assumes the blend to be incompressible and considers only uncorrelated (*i.e.*, random mixing assumption) copolymer-copolymer interactions. On the other hand, the pedestrian copolymer LCT [16] involves two significant improvements beyond the copolymer FH approximation. The first improvement lies in describing the uncorrelated interactions in terms of more realistic interactions between the united atom groups that are used to represent the monomer structures. As a second improvement, the theory is augmented with a temperature-independent contribution χ_s to the effective interaction parameter χ. This χ_s is determined explicitly (with no adjustable parameters) from the copolymer lattice cluster theory in the incompressible, athermal, fully flexible, long-chain limit. For example, the copolymer χ_s is found [17] to dominate the temperature-dependent portion of χ in binary blends of norbornene-co-ethylene random copolymers. In spite of its simplicity, the pedestrian random copolymer theory [16] enables the successful interpretation of a large body of data that cannot be explained with random copolymer FH theory. In addition to the norbornene-co-ethylene random copolymer mixtures already cited, these applications include ones to isotopic blends of saturated and unsaturated polybutadienes and to blends of ethylene-co-α-alkene random copolymers with sPB [16]. The polybutadiene isotopic blends are interesting in displaying a transition from upper to lower critical solution temperature behavior as the chain microstructure (*i.e.*, the copolymer compositions) is varied [18].

Our previous work [19] for binary homopolymer blends indicates, however, the importance of nonrandom mixing contributions to the LCT free energy, even in the enormously simplifying limit of high pressures and high molecular weights. These nonrandom mixing terms provide a correction to the number of heterocontacts due to the packing constraints imposed by the polymer chain connectivity and by monomer structures and represent a generalization of the mathemathically rather vague Guggenheim "surface fraction" concept [20,21] to a structured monomer homopolymer blend [19]. Thus, it is quite desirable to generalize this LCT pedestrian treatment to a copolymer blend by extending the existing LCT pedestrian approach [16] for copolymer blends beyond the random mixing assumption for the interactions. As we demonstrate here, this extension leads to a monomer sequence dependence of the free energy without the addition of new adjustable parameters.

Section 1) describes the extended lattice model and the basic features of the LCT for more general case of compressible systems. Section 2) specializes the theory to the high molecular weight, incompressible system limit of the LCT for binary blends of arbitrary copolymers (diblock, alternating, completely random, *etc.*), while section 3) further specializes this limiting theory to isotopic blends of two purely random copolymers. The theory is illustrated by considering the effective interaction parameter χ and the phase boundaries for isotopic polybutadiene blends, where the miscibility pattern departs qualitatively from the patterns assessible to random copolymer Flory-Huggins theory [2,3].

RESULTS

1. Extended Lattice Model and LCT: The extended lattice model of polymer systems rectifies a significant deficiency of the standard lattice model that requires a single monomer to occupy only a single lattice site. While this single site occupancy constraint emerges as a natural consequence of treating the monomers as structureless, entropically identical, indistinguishable entities, molecules of different chemical species are not structurally identical and exhibit a wide variety of sizes and shapes, even within a homologous series. Including the basic structural characteristics of monomers into a lattice theory clearly produces a more realistic modeling of polymer systems, in spite of the obvious limitations imposed by the descrete lattice morphology. The LCT combines this more realistic description of monomer structure with a significantly improved solution of the extended model and generates analytical expressions for the free energy in a form suitable for the complete thermodynamic analysis of diverse polymer systems [22].

When applied to binary blends of two copolymers, designated as A_xB_{1-x} and C_yD_{1-y}, this extended lattice model represents the individual monomers of species A, B, C, and D with structures composed, respectively, of s_A, s_B, s_C, and s_D submonomer units, each of which occupies a single lattice site. Consequently, the athermal limit of the noncombinatorial entropy for this copolymer blend is nonzero and depends explicitly on both the structural details of monomers and on the copolymer compositions x and y. This combinatorial entropy is almost entirely absent when the monomers A, B, C, and D are treated in the traditional manner as structureless entities. The values of s_A, s_B, s_C, and s_D are, generally, chosen to reflect relative monomer sizes. In the case of polyolefins, for instance, these single lattice site submonomer units are selected as CH_n ($n = 0,1,2$, or 3) united atom groups.

A single A_xB_{1-x} copolymer chain (called component 1 below) consists, on average, of n_A monomers of species A and n_B monomers of species B that are both distributed along the A_xB_{1-x} chain backbone, while a single C_yD_{1-y} chain (called component 2 below) contains n_C monomers of species C and n_D monomers of species D that are placed along the C_yD_{1-y} chain backbone. For simplicity, both the A_xB_{1-x} and C_yD_{1-y} chains are taken as compositionally monodisperse copolymers with the uniquely specified monomer fractions $x = n_A/(n_A + n_B)$ and $y = n_C/(n_C + n_D)$. The individual monomers in an A_xB_{1-x} chain are joined to each other by $(n_A + n_B - 1)$ backbone bonds. For a purely random A_xB_{1-x} copolymer, there are $x(n_A - 1)$ connecting bonds between successive AA monomers, $(1 - x)(n_B - 1)$ connecting bonds between BB pairs, and $2xn_B$ junction bonds between AB or BA monomers. Similarly, the number of connecting bonds in a purely random C_yD_{1-y} chain equals $(n_C + n_D - 1)$, and these bonds link CC, DD, and CD pairs with a total of $y(n_C - 1)$, $(1-y)(n_D - 1)$, and $2yn_D$ bonds, respectively. The chain occupancy indices M_1 and M_2 are defined as sums of products of corresponding numbers of monomers $\{n_\alpha\}$ and their occupancy indices $\{s_\alpha\}$ ($\alpha \equiv$ A,B,C,D), yielding $M_1 \equiv M_A + M_B = n_As_A + n_Bs_B$ and $M_2 \equiv M_C + M_D = n_Cs_C + n_Ds_D$. The binary copolymer blend is represented as a set of n_1 and n_2 A_xB_{1-x} and C_yD_{1-y} chains, respectively, residing on a three-dimensional cubic lattice with N_l lattice sites and a cordination number $z = 6$.

Excess free volume in compressible descriptions of the blend is modeled by the presence of n_v empty sites with a volume fraction $\phi_v = n_v/N_l = 1 - (n_1M_1 + n_2M_2)/N_l = 1 - \phi_1 - \phi_2$, where ϕ_1 and ϕ_2 are the actual volume fractions of two blend species and where ϕ_v is determined as a function of pressure, temperature, and composition from the equation of state. The unit of free volume is the volume associated with a single empty lattice site, that is, thus, much smaller than the monomer volumes, another realistic feature of the LCT that is absent in various generalization [23,24] of FH theory to compressible systems.

Endowing monomers with molecular structures also provides an improved representation of monomer-monomer interactions. No two united atom groups may occupy the same lattice site, and all united atom groups of species α and β on neighboring lattice sites interact with the (monomer averaged) attractive van der Waals energy $\varepsilon_{\alpha\beta}$. The minimal model, therefore, contains ten independent energies $\varepsilon_{\alpha\beta}$ for compressible A_xB_{1-x}/C_yD_{1-y} mixtures with $A \neq B \neq C \neq D$, while an even more realistic model with different (”specific”) interactions within a monomer yields considerably more energy parameters $\varepsilon_{\alpha\beta}^{(\gamma\delta)}$.

The extended lattice model of A_xB_{1-x}/C_yD_{1-y} blends is solved by using cluster expansion methods and by describing the influence of short range correlations from chain portions with as many as four bonds [11,14]. The presence of these short range correlations is responsible for nonrandom mixing and leads naturally within our approach to a monomer sequence and monomer structure dependence of computed thermodynamic properties. The Helmholtz free energy F of the copolymer blend is obtained as a perturbative expansion about the free energy $F^{(FH)}$ generated from a modified FH theory in which the blend is treated as compressible and in which the uncorrelated (*i.e.*, determined by random mixing) monomer-monomer interactions are described in terms of the interactions between united atom groups or monomer portions. The LCT free energy F is written formally as

$$\frac{F}{N_l k_B T} = \frac{F^{(FH)}}{N_l k_B T} + \text{corrections} \tag{1}$$

where the corrections to $F^{(FH)}$ are derived [11,14] as polynomials in the actual volume fractions ϕ_1 and ϕ_2. When one or both of the blend components contains a random or quasi-random distribution of monomers along the chain backbone, these free energy corrections must be averaged over a statistical distribution of all possible monomer sequences for all chains in the system, an averaging that makes the calculations *extremely* tedious. Technical details and the diagramatic representation of F are partially described [14] elsewhere.

2. High molecular weight, incompressible limit of LCT: While the LCT approximation for the corrections in (1) is algebrically lengthy and suitable only for numerical analysis, considering the high molecular weight, incompressible limit of the LCT enormously simplifies the algebra and produces rather compact and physically revealing formulas for the thermodynamic properties of homopolymer binary blends [19]. Thus, we apply this same limit to binary A_xB_{1-x}/C_yD_{1-y} copolymer blends to achieve the maximum degree of the algebraic simplicity and physical insights. Let $\phi \equiv \phi_1 = 1 - \phi_2$ designate the composition of the incompressible blend. In the incompressible, long chain limit, the Helmholtz free energy of mixing ΔF^{mix} for the A_xB_{1-x}/C_yD_{1-y} copolymer blend takes the form,

$$
\begin{aligned}
\frac{\Delta F^{mix}}{N_l k_B T} = {} & \frac{\phi}{M_1}\ln\phi + \frac{1-\phi}{M_2}\ln(1-\phi) + \phi(1-\phi)\Bigg\{ \frac{1}{z^2}\left[\frac{N_1^{(2)}}{M_1} - \frac{N_2^{(2)}}{M_2}\right]^2 + \\
& \left(\frac{\overline{\varepsilon}}{k_B T}\right)\left(\frac{z-2}{2} - \frac{1}{z}\left[\frac{N_1^{(3)}}{M_1}\phi + \frac{N_2^{(3)}}{M_2}(1-\phi)\right]\right) + \\
& \frac{2}{z}\left[\frac{\overline{\varepsilon_{11}}}{k_B T} - \frac{\overline{\varepsilon_{12}}}{k_B T}\right]\frac{N_1^{(3)}}{M_1} + \frac{2}{z}\left[\frac{\overline{\varepsilon_{22}}}{k_B T} - \frac{\overline{\varepsilon_{12}}}{k_B T}\right]\frac{N_2^{(3)}}{M_2} + \Delta_1 + \Delta_2 \Bigg\}
\end{aligned}
\qquad (2)
$$

where the subscripts 1 and 2 label the blend components, the geometrical coefficient $N_i^{(k)}$ ($i = 1,2$) denotes the number of runs of k sequential bonds (see below) in a single chain of component i, and where the interaction energy parameters $\overline{\varepsilon_{i,j}}$ are particular linear combinations of the nearest neighbor van der Waals attractive energies $\varepsilon_{\alpha\beta}$ ($\alpha,\beta \equiv A, B, C, D$),

$$
\overline{\varepsilon_{ij}} = \varepsilon_{\gamma\lambda} m_\gamma^{(i)} m_\lambda^{(j)} + \varepsilon_{\gamma\mu} m_\gamma^{(i)} m_\mu^{(j)} + \varepsilon_{\delta\lambda} m_\delta^{(i)} m_\lambda^{(j)} + \varepsilon_{\delta\mu} m_\delta^{(i)} m_\mu^{(j)}, \quad i,j = 1, 2, \qquad (3)
$$

with the pairs (γ,δ) and (λ,μ) labeling the two different monomer species in chains of components i and j, respectively. The statistical weights $m_\alpha^{(i)}$ in (3) represent the fractions of the M_i united atom groups in a single chain of component i ($i = 1,2$) that belong to species α ($\alpha \equiv A, B, C, D$). Thus, we simply have $m_\alpha^{(i)} = M_\alpha/M_i = n_\alpha s_\alpha/M_i$. The product $m_A^{(1)} m_A^{(1)}$, for instance, is proportional to the contact probability for interactions between uncorrelated (*i.e.* randomly mixed) AA submonomer units, and $\overline{\varepsilon_{11}}$ is a statistically averaged interaction energy between a pair of submonomer units belonging to the copolymer species 1. The energy $\overline{\varepsilon}$ of (2) is the exchange energy for the copolymer blend and is determined from the energies $\{\overline{\varepsilon_{ij}}\}$ in the standard fashion of,

$$
\overline{\varepsilon} = \overline{\varepsilon_{11}} + \overline{\varepsilon_{22}} - 2\overline{\varepsilon_{12}} \qquad (4)
$$

The last two terms in (2) are the monomer sequence dependent contributions given by

$$
\Delta_1 = -\frac{2}{z}\left[\frac{\varepsilon_{A-(1)}}{k_B T} - \frac{\varepsilon_{A-(2)}}{k_B T}\right]\frac{N_1^{(3)}(A \cdots A)}{M_1} - \frac{2}{z}\left[\frac{\varepsilon_{B-(1)}}{k_B T} - \frac{\varepsilon_{B-(2)}}{k_B T}\right]\frac{N_1^{(3)}(B \cdots B)}{M_1}
$$

$$-\frac{1}{z}\left[\frac{\varepsilon_{A-(1)}}{k_BT}-\frac{\varepsilon_{A-(2)}}{k_BT}+\frac{\varepsilon_{B-(1)}}{k_BT}-\frac{\varepsilon_{B-(2)}}{k_BT}\right]\frac{N_1^{(3)}(A\cdots B)}{M_1}$$

$$+\frac{1}{z}\left[\frac{\varepsilon_{A-(1)}}{k_BT}-\frac{\varepsilon_{B-(1)}}{k_BT}\right]\left[\frac{N_1^{(2)}(B-B-A)}{M_1}-\frac{N_1^{(2)}(A-A-B)}{M_1}\right] \tag{5}$$

and

$$\Delta_2=-\frac{2}{z}\left[\frac{\varepsilon_{C-(2)}}{k_BT}-\frac{\varepsilon_{C-(1)}}{k_BT}\right]\frac{N_2^{(3)}(C\cdots C)}{M_2}-\frac{2}{z}\left[\frac{\varepsilon_{D-(2)}}{k_BT}-\frac{\varepsilon_{D-(1)}}{k_BT}\right]\frac{N_2^{(3)}(D\cdots D)}{M_2}$$

$$-\frac{1}{z}\left[\frac{\varepsilon_{C-(2)}}{k_BT}-\frac{\varepsilon_{C-(1)}}{k_BT}+\frac{\varepsilon_{D-(2)}}{k_BT}-\frac{\varepsilon_{D-(1)}}{k_BT}\right]\frac{N_2^{(3)}(C\cdots D)}{M_2}$$

$$+\frac{1}{z}\left[\frac{\varepsilon_{C-(2)}}{k_BT}-\frac{\varepsilon_{D-(2)}}{k_BT}\right]\left[\frac{N_2^{(2)}(D-D-C)}{M_2}-\frac{N_2^{(2)}(C-C-D)}{M_2}\right] \tag{6}$$

where the energy parameter $\varepsilon_{\alpha-(i)}$ specifies an averaged interaction energy between a single united atom group of the species α and an averaged one of component i,

$$\varepsilon_{\alpha-(i)}=\varepsilon_{\alpha\gamma}m_\gamma^{(i)}+\varepsilon_{\alpha\delta}m_\delta^{(i)},\quad i=1,2,\quad \alpha=A,B,C,D \tag{7}$$

with the subscripts γ and δ again representing the monomer species of the component i (when $i=1$, $\gamma\equiv A$ and $\delta\equiv B$, while for $i=2$, $\gamma\equiv C$ and $\delta\equiv D$).

The monomer sequence dependent geometrical factors $N_i^{(3)}(X\cdots Y)$ of (5) and (6) enumerate the number of configurations of three sequential bonds (called tetramers) in a single chain of component i that have X and Y submonomer units at the ends of the tetramer ($X,Y\in\{A,B\}$ for $i=1$ and $X,Y\in\{C,D\}$ for $i=2$). The notation $N_i^{(2)}(X\!-\!X\!-\!Y)$ designates the number of configurations of two sequential bonds (in a single chain of component i) that link three united atom groups with the specific connectivity in which X is bonded to X, and the middle X is bonded to Y. Note that the coefficients $N_i^{(k)}$, $N_i^{(k)}(X\cdots Y)$, and $N_i^{(k)}(X\!-\!X\!-\!Y)$ all depend on the composition of the copolymer component i as well as on the statistics of the sequence distribution. The next section and the Appendix illustrate the evaluation of the geometrical factors $N_i^{(k)}$, $N_i^{(k)}(X\cdots Y)$, and $N_i^{(k)}(X\!-\!X\!-\!Y)$ for random copolymers. Within the incompressible, long chain limit of the LCT for A_xB_{1-x}/C_yD_{1-y} mixtures (with $A \neq B \neq C \neq D$), the number of independent interaction energies, which are the adjustable parameters of the theory, is reduced to eight from the ten parameters present in the minimal theory for compressible systems. Of course, when C=A or B, *etc.*, the number of energy parameters diminishes.

Equation (2) is presented in a general form that describes blends of random copolymers, diblock copolymers, alternating copolymers, as well as of copolymers with kinetically controlled monomer sequences. The differences between all these copolymer systems appear in the Δ_1 and Δ_2 terms through the explicit dependence of the geometrical coefficients $N_i^{(k)}(X \cdots Y)$, and $N_i^{(k)}(X-X-Y)$ of (5) and (6) on the monomer sequence distribution. There is no need for extra adjustable parameters to represent the sequence dependence. The remaining terms of (2) are common for all types of copolymers. In particular, the first two terms on the right-hand side of (2) represent the configurational entropy, while the contribution $\phi(1-\phi)[N_1^{(2)}/M_1 - N_2^{(2)}/M_2]^2/z^2$ is the noncombinatorial entropy of mixing which arises from nonrandom mixing effects associated with packing chains that have monomers of different sizes and shapes and, generally, different compositions x and y. The sequence independent ratios $r_i \equiv N_1^{(2)}/M_i$ for the A_xB_{1-x} and C_yD_{1-y} copolymers may be expressed more conveniently as [16]

$$r_1 \equiv \frac{N_1^{(2)}}{M_1} = \frac{[s_A + s_A^{(tri)} + 3s_A^{(tetr)}]x + [s_B + s_B^{(tri)} + 3s_B^{(tetr)}](1-x)}{s_A x + s_B(1-x)} \tag{8}$$

and

$$r_2 \equiv \frac{N_2^{(2)}}{M_2} = \frac{[s_C + s_C^{(tri)} + 3s_C^{(tetr)}]y + [s_D + s_D^{(tri)} + 3s_D^{(tetr)}](1-y)}{s_C y + s_D(1-y)} \tag{9}$$

where $s_\alpha^{(tri)}$ and $s_\alpha^{(tetr)}$ are the numbers of tri- and tetrafunctional united atom groups in a single monomer of species α and where the $M_i \to \infty$ limit has been invoked. This entropic contribution is contained in the pedestrian LCT theory [16]. The remaining terms in (2) are of energetic origin as discussed below.

The incompressible limit SANS χ parameter is defined through the free energy of mixing ΔF^{mix} as

$$\left.\frac{\partial^2(\Delta F^{mix}/N_l k_B T)}{\partial \phi^2}\right|_{T,V} = \frac{1}{M_1\phi} + \frac{1}{M_2(1-\phi)} - 2\chi_{site} \tag{10}$$

where the subscript *site* on χ_{site} indicates that the χ parameter is expressed per lattice site (or, equivalently, as an interaction parameter between united atom groups). The usual experimental SANS χ is obtained from the extrapolated zero-angle scattering internsity $I(0)$ as

$$\chi_{exp} = \left(\frac{\nu_0}{2}\right)\left[\frac{1}{N_1\nu_1\phi_1} + \frac{1}{N_2\nu_2\phi_2} - \frac{k_N}{I(0)}\right] \tag{11}$$

where N_i and ν_i are the polymerization index and the molar monomer volume of component i, respectively, k_N is the scattering contrast factor, and ν_0 is an arbitrary chosen normalization volume. The theoretical and experimental χ parameters of (10) and (11) are related to each other by a simple scaling [16,25],

$$\chi_{exp} = c\chi_{site} \tag{12}$$

with the conversion factor c equaling $c = s_1s_2/[s_1(1 - \phi) + s_2\phi]$ when choosing $\nu_0 = [\phi/\nu_1 + (1 - \phi)/\nu_2]^{-1}$ and being $c = (s_1s_2)^{1/2}$ for the simpler choice of $\nu_0 = (\nu_1\nu_2)^{1/2}$.

Evaluating the free energy derivative in (10) converts it into the slightly more compact form,

$$\chi_{site} = \frac{1}{z^2}\left[\frac{N_1^{(2)}}{M_1} - \frac{N_2^{(2)}}{M_2}\right]^2 + \left(\frac{\overline{\varepsilon}}{kT}\right)\left(\frac{z-2}{2} + \frac{1}{z}\left[\frac{N_1^{(3)}}{M_1}[1-3(1-\phi)] + \frac{N_2^{(3)}}{M_2}(1-3\phi)\right]\right) + \frac{2}{z}\left[\frac{\overline{\varepsilon}_{11}}{k_BT} - \frac{\overline{\varepsilon}_{12}}{k_BT}\right]\frac{N_1^{(3)}}{M_1} + \frac{2}{z}\left[\frac{\overline{\varepsilon}_{22}}{k_BT} - \frac{\overline{\varepsilon}_{12}}{k_BT}\right]\frac{N_2^{(3)}}{M_2} + \Delta_1 + \Delta_2 \tag{13}$$

The first term on the right-hand side of (13) is the athermal limit entropic component of χ_{site} that depends only on the monomer structures of the two copolymer blend components and on their compositions x and y. The remaining terms are the temperature-dependent contributions. The Flory-Huggins-Guggenheim (FH-G) type term $\overline{\varepsilon}(z-2)/(2k_BT)$ describes the interactions between uncorrelated united atom groups and is the energetic portion of the simpler pedestrian random copolymer LCT. The second term with the overall factor of $\overline{\varepsilon}/k_BT$ contains both composition *dependent* and independent portions. This second term provides a correction to the random mixing (FH-G) approximation due to the packing constraints imposed by the fact that the two copolymer components are structurally different (*i.e.* have different monomer structures and different compositions). The remaining four terms of (13) represent a correction to the temperature dependent portion of χ_{site} that arises from the energetic and structural heterogeneity of all copolymer chains. These terms are absent for an A/C binary homopolymer blend and therefore vanish identically if we set B ≡ A and D ≡ C in (3–7) and (13). The monomer sequence dependence of χ_{site} enters through the Δ_1 and Δ_2 which differ for alternating, diblocks, or random copolymers of the same monomer compositions.

3. Isotopic mixtures of unsaturated (or saturated) polybutadienes: Isotopic blends are the simplest examples of A_xB_{1-x}/C_yD_{1-y} binary copolymer blends since the monomers A and C (as well as B and D) have identical structures and differ only in the interaction energies $\{\varepsilon_{\alpha\beta}\}$ due to the replacement of the hydrogen atoms by deuterium. This feature significantly reduces the number of adjustable interaction parameters and, thus, provides ideal systems for testing theoretical predictions. We now specialize to an isotopic blend of polybutadienes as a widely studied system [18, 26–28]. Let component 1 designate a purely random A_xB_{1-x} copolymer with a fraction x of perdeuterated 1,2 units and a fraction $(1-x)$ of perdeuterated 1,4 units, whereas component 2 denotes a statistical copolymer C_yD_{1-y} of hydrogenated 1,2 and 1,4 PB monomers.

Figure 1 depicts the obvious united atom monomer structures for 1,2 and 1,4 monomers in the two blend components. Noticing from Figure 1 that the monomer structures for PB 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 (8) and (9) simplify to

$$r_1 = \frac{(4+1)x + 4(1-x)}{4x + 4(1-x)} = \frac{x+4}{4} \tag{14}$$

and

$$r_2 = \frac{(4+1)y + 4(1-y)}{4y + 4(1-y)} = \frac{y+4}{4} \tag{15}$$

As shown in the Appendix, the ratios $p_i \equiv N_i^{(3)}/M_i$ $(i = 1,2)$ of (13) and the ratios $p_i^{(X,Y)} \equiv N_i^{(3)}(X \cdots Y)/M_i$ and $r_i^{(X-X-Y)} \equiv N_i^{(2)}(X-X-Y)/M_i$ of (5) and (6) can likewise be expressed for PB blends in the long chain limit $(M_i \to \infty)$ as simple polynomials in the composition of the purely random copolymer component i,

$$p_1 = \frac{4+2x}{4}, \qquad p_2 = \frac{4+2y}{4} \tag{16}$$

$$p_1^{(A\cdots A)} = \frac{x + 4x^2 + x^3}{4}, \qquad p_2^{(C\cdots C)} = \frac{y + 4y^2 + y^3}{4} \tag{17}$$

$$p_1^{(B\cdots B)} = \frac{x - 6x + x^2 + x^3}{4}, \qquad p_2^{(D\cdots D)} = \frac{x - 6y + y^2 + y^3}{4} \tag{18}$$

$$p_1^{(A\cdots B)} = \frac{7x - 5x^2 - 2x^3}{4}, \qquad p_2^{(C\cdots D)} = \frac{7y - 5y^2 - 2y^3}{4} \tag{19}$$

$$r_1^{(A-A\sim B)} = \frac{3x - 3x^2}{4}, \qquad r_2^{(C-C\sim D)} = \frac{3y - 3y^2}{4} \tag{20}$$

and

$$r_1^{(A\sim B-B)} = \frac{2x - 2x^2}{4}, \qquad r_2^{(C\sim D-D)} = \frac{2y - 2y^2}{4} \tag{21}$$

The notation $X - X \sim Y$ of (20) and (21) distinguishes the connecting bonds $X \sim Y$ by wiggly lines ~, while the bonds $X - X$ lying inside the monomers are denoted by solid lines –.

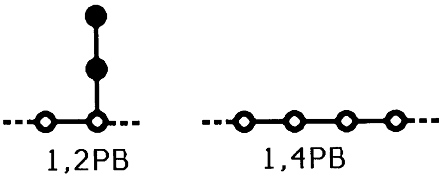

Figure 1. United atom structures for 1,2 and 1,4 polybutadiene (PB) monomers. Open circles denote united atom groups belonging to the chain backbone, while filled circles indicate the side groups.

In order to reduce the number of adjustable parameters to the bare minimum, we assume that there are only three independent microscopic van der Waals energies ε_{CC}, ε_{DD}, and ε_{CD} representing interactions between two hydrogenated 1,2-1,2, 1,4-1,4, and 1,2-1,4 CH_n groups, respectively. The remaining seven energy parameters are determined by using simple scaling relations in the spirit of the polarizability model of Bates *et al.* [29],

$$\varepsilon_{AA} = \gamma^2 \varepsilon_{CC}, \qquad \varepsilon_{BB} = \gamma^2 \varepsilon_{DD}, \qquad \varepsilon_{AB} = \gamma^2 \varepsilon_{CD} \tag{22}$$

and

$$\varepsilon_{AC} = \gamma \varepsilon_{CC}, \qquad \varepsilon_{BD} = \gamma \varepsilon_{DD}, \qquad \varepsilon_{AD} = \varepsilon_{BC} = \gamma \varepsilon_{CD} \tag{23}$$

where the scaling factor γ is less than unity, to reflect the weaker attraction of the deuterated species, and γ is taken, for simplicity, as the same for the 1,2 and 1,4 units. The identity of the monomer occupancy indices s_α in both blend components ($s_A = s_B$ and $s_C = s_D$) implies that the statistical weights $m_\alpha^{(i)}$ coincide with the corresponding copolymer compositions,

$$m_A^{(1)} = 1 - m_B^{(1)} = x, \qquad \text{and} \qquad m_C^{(2)} = 1 - m_D^{(2)} = y \tag{24}$$

Substituting (14–24) into (3–9) and the latter into (13) produces, after some algebra, the interaction parameter χ_{site} as a function of three van der Waals energies $\varepsilon_{CC,}$ ε_{DD}, and ε_{CD}, the deuterium-hydrogen scaling factor γ, the random copolymer compositions x and y, and the blend composition ϕ,

$$\begin{aligned}
\chi_{site} = {} & \frac{1}{576}[x-y]^2 + \frac{1}{24}\left[\frac{\varepsilon_{CC}}{k_BT} + \frac{\varepsilon_{DD}}{k_BT} - 2\frac{\varepsilon_{CD}}{k_BT}\right]\{(-2+6\phi)\gamma^2x^3 + (4-6\phi)y^3 + \\
& + [(2-6\phi)\gamma^2 + (7-12\phi)\gamma]x^2y + [(-5+12\phi)\gamma - 4 + 6\phi)]xy^2 + 42[\gamma x - y]^2 - 2\gamma xy\} \\
& + \frac{1}{24}\left[\frac{\varepsilon_{CD}}{k_BT} - \frac{\varepsilon_{DD}}{k_BT}\right]\{[(-6+12\phi)\gamma^2 + (7-12\phi)\gamma]x^2 + [(-5+12\phi)\gamma + 6 - 12\phi]y^2 \\
& + 4[(1-3\phi)\gamma^2 + \gamma - 2 + 3\phi]xy + [86\gamma^2 - 87\gamma]x + [-87\gamma + 86]y\} \\
& + \frac{1}{24}\left[\frac{\varepsilon_{DD}}{k_BT}\right](1-\gamma)^2[44 + (-4+6\phi)x + (2-6\phi)y]
\end{aligned} \tag{25}$$

Equation (25) departs significantly from that obtained from our simple extension [16] of Flory-Huggins random copolymer theory that includes a temperature independent portion of the interaction parameter and that describes the random mixing interaction energy in terms of united atom interactions,

$$\begin{aligned}
\chi'_{site} = {} & \frac{1}{576}[x-y]^2 + 3\left\{\left[\frac{\varepsilon_{CC}}{k_BT} + \frac{\varepsilon_{DD}}{k_BT} - 2\frac{\varepsilon_{CD}}{k_BT}\right][\gamma x - y]^2 + \left[\frac{\varepsilon_{CD}}{k_BT} - \frac{\varepsilon_{DD}}{k_BT}\right]\right. \\
& \left. 2\gamma(\gamma-1)(\gamma x - y) + \left[\frac{\varepsilon_{DD}}{k_BT}\right](1-\gamma)^2\right\}
\end{aligned} \tag{26}$$

(The coefficient $z/2 = 3$ that multiplies the overall energy term in (26) should be replaced by $(z-2)/2 = 2$ for comparison with (25) Firstly, the χ_{site} from the LCT "pedestrian" approach of (25) depends on the blend composition ϕ. Secondly, χ_{site} exhibits a much richer dependence on compositions x and y than χ'_{site} of (26), and, finally, χ_{site}

contains sequence dependent contributions arising from the completely random character of the two copolymers, *i.e.*, from their statistically averaged monomer sequences. For symmetric isotopic PB blends ($\phi = 0.5$), (25) simplifies to,

$$\chi_{site} = \frac{1}{576}[x-y]^2 + \frac{1}{24}\left[\frac{\varepsilon_{CC}}{k_BT} + \frac{\varepsilon_{DD}}{k_BT} - 2\frac{\varepsilon_{CD}}{k_BT}\right]\{\gamma^2 x^3 + y^3 + \gamma(1-\gamma)x^2 y - (1-\gamma)xy^2$$

$$+ 42[\gamma x - y]^2 - 2\gamma xy\} + \frac{1}{24}\left[\frac{\varepsilon_{CD}}{k_BT} - \frac{\varepsilon_{DD}}{k_BT}\right]\{\gamma x^2 + \gamma y^2 - 2(1-\gamma)^2 xy + [86\gamma^2 - 87\gamma]x$$

$$+ [-87\gamma + 86]y\} + \frac{1}{24}\left[\frac{\varepsilon_{DD}}{k_BT}\right](1-\gamma)^2[44 - x - y] \tag{27}$$

Setting $\gamma = 1$ in (27) yields the LCT interaction parameter χ_{site} for a symmetric ($\phi = 0.5$) C_xD_{1-x}/C_yD_{1-y} polybutadiene blend,

$$\chi_{site} = \frac{1}{576}[x-y]^2 + \frac{1}{24}\left[\frac{\varepsilon_{CC}}{k_BT} + \frac{\varepsilon_{DD}}{k_BT} - 2\frac{\varepsilon_{CD}}{k_BT}\right]\{x^3 + y^3 + 42(x-y)^2 - 2xy\}$$

$$+ \frac{1}{24}\left[\frac{\varepsilon_{CD}}{k_BT} - \frac{\varepsilon_{DD}}{k_BT}\right]\{x^2 + y^2 - x - y\} \tag{28}$$

As evident from (28), the effective interaction parameter χ_{site} for a mixture of two identical PB random copolymers (varying only in the percentage of 1,2 and 1,4 addition units) depends on two adjustable parameters, the exchange energy $\varepsilon = \varepsilon_{CC} + \varepsilon_{DD} - 2\varepsilon_{CD}$ for the C/D binary homopolymer blend and the van der Waals energy difference $\Delta\varepsilon = \varepsilon_{CD} - \varepsilon_{DD}$. Equation (28) differs considerably from the well known formula of FH random copolymer theory [2,3],

$$\chi_{site}^{(FH)} = \frac{z}{2}\left[\frac{\varepsilon_{CC}}{k_BT} + \frac{\varepsilon_{DD}}{k_BT} - 2\frac{\varepsilon_{CD}}{k_BT}\right][x-y]^2 \tag{29}$$

The differences between (29) and (28) become more transparent when (28) is rewritten in a form that maintains symmetry between the energies ε_{CC} and ε_{DD},

$$\chi_{site} = \frac{1}{576}[x-y]^2 + \left[\frac{\varepsilon_{CC}}{k_BT} + \frac{\varepsilon_{DD}}{k_BT} - 2\frac{\varepsilon_{CD}}{k_BT}\right][x-y]^2\left[\frac{11}{6} - \frac{x}{24} - \frac{y}{24}\right]$$

$$+\frac{1}{24}\left[\frac{\varepsilon_{CC}}{k_BT} - \frac{\varepsilon_{CD}}{k_BT}\right][2x^3 + 2y^3 - x^2y - xy^2 - 2x^2 - 2y^2 + 2xy]$$

$$+\frac{1}{24}\left[\frac{\varepsilon_{DD}}{k_BT} - \frac{\varepsilon_{CD}}{k_BT}\right][2x^3 + 2y^3 - x^2y - xy^2 - 3x^2 - 3y^2 + 2xy + x + y] \qquad (30)$$

A knowledge of the interaction parameter χ_{site} enables computing phase boundaries from the standard stability condition,

$$\frac{1}{M_1\phi} + \frac{1}{M_2(1-\phi)} - 2\chi_{site} = 0 \qquad (31)$$

for incompressible binary systems. Figure 2 depicts a few examples of the spinodal curves $y(T = \text{const}, \phi = \text{const}) = y(x)$ for isotopic unsaturated polybutadiene blends. The polymerization indices for both random PB copolymers are assumed to be identical and equal, $N_1 = N_2 = 10^3$, while the microscopic van der Waals energies ε_{CC}, ε_{DD}, and ε_{CD} and the scaling deuterium-hydrogen factor γ are taken from our previous fits [25] of (26) to the SANS data of Jinnai *et al.* [18] for these mixtures. Although we do not expect that these four adjustable parameters would change substantially if the new (25) is used instead in the fitting procedure, the examples of Figure 2 should be treated as illustrations of general trends rather than as quantitative predictions. The three spinodal curves in Figure 2 correspond to three different blend compositions $\phi = 0.5$, $\phi = 0.25$, and $\phi = 0.15$. The phase boundaries for the compositions $\phi = 0.75$ and $\phi = 0.85$ have been found to be very similar to those for the respective symmetrical compositions $\phi = 0.25$ and $\phi = 0.15$ and, therefore, are not shown in the figure. The region inside the loop represents an *immiscibility* window, which shrinks more as ϕ departs further from the symmetrical value of $\phi = 0.5$. Far away from the diagonal $y = x$, χ_{site} is negative, and the system is miscible; closer to $y = x$, the interaction parameter χ_{site} changes its sign to positive and produces an immiscibilty window from the competition with the positive entropic terms. Preliminary calculations for isotopic blends of the saturated polybutadienes yield a miscibility window that borders around the diagonal $y = x$ in qualitative accord with predictions of random copolymer FH theory.

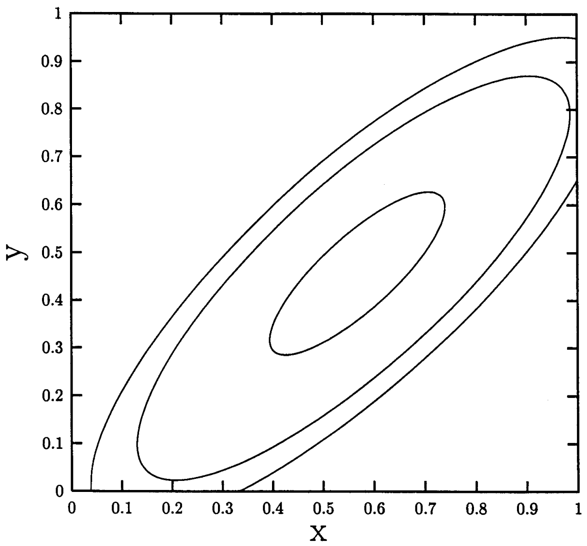

Figure 2. Phase boundaries $y(T = \text{const}, \phi = \text{const}) = y(x)$ for the miscibility of the isotopic polybutadienes blends for three different blend compositions $\phi = 0.5$, 0.25, and 0.15. The smallest closed loop immiscibility window refers to the lowest composition $\phi = 0.15$, while the largest loop corresponds to $\phi = 0.5$. The temperature is chosen as $T = 450$ K and the polymerization indices of the two PB random copolymers are assumed to be $N_1 = N_2 = 10^3$ for all three blend samples. The deuterium-hydrogen scale factor γ and the van der Waals energies ε_{CC}, ε_{DD}, and ε_{CD} have been taken from our previous fit [25] of (26) to the SANS data of Jinnai *et al.* [18], but the $\{\varepsilon_{\alpha\beta}\}$ are rescaled by a factor $z/(z-2)$ (with $z = 6$) to account for the presence of two different proportionality coefficients between the exchange energy ε and the effective interaction parameter χ_{site} in (25) and (26). Thus, we use $\varepsilon_{CC} = z/(z-2) \times 390.24$ K, $\varepsilon_{DD} = z/(z-2) \times 406.85$ K, and $\varepsilon_{CD} = z/(z-2) \times 398.46$ K. The deuterium-hydrogen scale factor $\gamma = 0.987$ is taken as unchanged.

DISCUSSION

A new version of the copolymer lattice cluster theory is developed to describe binary blends of two structured monomer copolymers in the simplifying limit of an incompressible system and high molecular weights. This version represents a significant improvement over our previous extension [16] of the random copolymer FH theory which, in turn, contains two significant advances over prior Flory-Huggins type random copolymer theories. The present extension combines these two previous advancements with another major improvement. The two advances in our previous "pedestrian" LCT for random copolymers are: a) the definition of polymer-polymer interactions in terms of the more realistic interactions between united atom groups and b) the explicit addition of the temperature independent portion χ_s of the effective interaction parameter χ (with no adjustable parameters) which is evaluated from the lattice cluster theory in the simplifying incompressible system, athermal, fully flexible, long chain limit. The present modification of the theory lies in including the ever present nonrandom mixing effects which, in turn, lead to a composition and monomer structure dependence of the contact probabilities for the effective interactions and to a monomer sequence dependence of the free energy without the addition of new adjustable parameters. Thus, the enthalpic portion of the effective χ parameter becomes composition and monomer sequence dependent.

The general theory of section 1 applies to blends containing random copolymer, diblock copolymers, alternating copolymers, as well as of copolymers with kinetically controlled monomer sequences, while section 2 illustrates the general theory for purely random copolymer blends of deuterated and hydrogenated polybutadienes. The calculated closed loop phase boundaries (in copolymer composition space) for these systems lie entirely outside the scope of classical FH random copolymer theory [2,3] which ignores the presence of χ_s. However, the application of the new theory requires the determination of several monomer structure and monomer sequence dependent geometrical factors, a process that is more complicated than calculating the geometrical coefficients in the corresponding pedestrian lattice cluster approach [19] for homopolymers blends. Nevertheless, the calculations of the geometrical factors (see Appendix) are fairly straighforward and yield rather compact algebraic expressions that are quite easy to apply.

Our new theory provides physical insights into the origin of the monomer sequence dependence of the free energy. Equations (5) and (6) demonstrate that this sequence dependence arises from sequentially bonded triads and tetrads of united atom groups lying on the same copolymer chain. For the polybutadiene example, this sequence dependence arises, as described [14] previously, from pairs of bonded monomers on a single chain, but with no added parameters. This represents a large departure from *ad hoc* extensions [8–10] of random copolymer Flory-Huggins theories that attempt to include a sequence dependence by introducing a set of parameters $\chi_{ijk,lmn}$ (or $\chi_{ij,kl}$) between triads (or diads) of monomers on two different copolymer chains. However, a more appropriate comparison with the assumptions of the phenomenological models [8–10] for the monomer sequence dependence is obtained when (5) and (6) are specialized to the case where all A, B, C, and D monomers of the A_xB_{1-x}/C_yD_{1-y} random copolymer mixture are represented by single bead entities (*i.e.*, all A, B, C, and D monomers each occupy single lattice sites). As a further simplification, we allow the two random copolymers to be identical (*i.e*, $A \equiv C$ and $B \equiv D$), apart from the compositions x and y. As expected, both sequence dependent terms Δ_1 and Δ_2 of (5) and (6) do not vanish. Our theory yields the monomer sequence dependence as steming from triads or tetrads of sequential monomers on a single chain. The energetic portion of the blend χ parameter calculated from Δ_1 and Δ_2 exhibits a richer dependence on the compositions x and y than of the conventional form $(x-y)^2$. The corrections $\Delta_1 + \Delta_2$ depend both on the exchange energy $\varepsilon = \varepsilon_{CC} + \varepsilon_{DD} - 2\varepsilon_{CD}$ and on the energy difference $\Delta\varepsilon = \varepsilon_{CD} - \varepsilon_{DD}$, thereby containing an extra parameter ($\Delta\varepsilon$) beyond random copolymer FH theory [2,3], albeit a parameter of clear physical origins and one that may be determined from independent measurements. This example suggests that the *ad hoc* physical idea [8] of triad-triad interactions as the molecular origins for the monomer sequence dependence of thermodynamic properties represents a step roughly in the correct direction, but our more rigorous approach introduces this sequence dependence through a proper evaluation of the copolymer "surface fractions". The final theory contains no new adjustable parameters beyond those already present for treating binary blends of homopolymers constituted from the monomers present in the copolymers chains.

Appendix

In order to evaluate the geometrical coefficients $p_i^{(X\cdots Y)} \equiv N_i^{(3)}(X\cdots Y)/M_i$ of (5) and (6), we distinguish between bonds connecting neighboring monomers (denoting them with wiggly lines ~) and bonds linking submonomers groups inside the monomers (designating them with solid lines –). Consider a single A_xB_{1-x} purely random copolymer chain which has, in addition to the A–A and B–B internal monomer bonds, $x(n_A-1)$, $(1-x)(n_B-1)$, and $2xn_B$ A ~ A, B ~ B, and A ~ B connecting bonds, respectively (where n_α is the number of monomers of species α in a single chain). The number of A–A–A–A configurations equals the number of monomers n_A since there is only one such configuration (containing all united atom groups in a 1,2 unit) in each monomer of species A. (See Figure 1 for the monomer structures for both A and B species). Likewise, we have $N_1^{(3)}$(B–B–B–B) = n_B for the 1,4 monomers. Table 1 provides the total numbers for all possible configurations of three sequential bonds when the structures for the A and B monomers are represented by the united atom groups model of Figure 1 and when the sequence distribution is purely random. The number of connecting bonds in each configuration of Table 1 ranges from zero to two. For a given bond pattern containing one or two connecting bonds, the corresponding $N_1^{(3)}$ (bond pattern) factor is the product of the number of connecting bonds in a single chain and the appriopriate symmetry number that reflects the connectivity of the internal monomers bonds in this pattern. For instance, we obtain $N_1^{(3)}$(A–A~A–A) = $2n_A(n_A-1)/(n_A+n_B)$ as follows: The number of A~A connecting bonds in a chain is obtained by multiplying the total number of connecting bonds in a chain, which is n_A+n_B-1, by the probability that both ends of a connecting bond belong to monomers of species A, which is $[n_A/(n_A+n_B)]\times[(n_A-1)/(n_A+n_B-1)]$. For each of the $n_A(n_A-1)/(n_A+n_B)$ connecting bonds A~A, the left hand side bond A–A may lie either in the chain backbone or in the side group of the 1,2 unit, while the right hand side bond A–A may be selected only from the chain backbone of the 1,2 monomer, *i.e.*, in only one way. Thus, the symmetry number equals 2 × 1 = 2.

Table 1. Monomer sequence dependent geometrical factors $N_1^{(3)}$(chain pattern), $N_1^{(2)}$(chain pattern), $p_1^{(\text{chain pattern})} \equiv \lim_{M_1\to\infty}[N_1^{(3)}(\text{chain pattern})/M_1]$, and $r_1^{(\text{chain pattern})} \equiv \lim_{M_1\to\infty}[N_1^{(2)}(\text{chain pattern})/M_1]$, for component 1 in the model of purely random copolymer PB blends. The monomer structures for the species A and B are depicted in Figure 1.

chain pattern of *k* bonds	$N_1^{(k)}$ (chain pattern)	$\lim_{M_1\to\infty}\left[\dfrac{N_1^{(k)}(\text{chain pattern})}{M_1}\right]$
A–A–A–A	n_A	$(1/4)x$
A–A~A–A	$2\dfrac{n_A(n_A-1)}{n_A+n_B}$	$(1/2)x^2$
A–A–A~A	$2\dfrac{n_A(n_A-1)}{n_A+n_B}$	$(1/2)x^2$
A~A–A~A	$\dfrac{n_A(n_A-1)(n_A-2)}{(n_A+n_B)(n_A+n_B-1)}$	$(1/4)x^3$
B–B–B–B	n_B	$(1/4)(1-x)$

Table 1 (continuation)

B–B~B–B	$\frac{n_B(n_B-1)}{n_A+n_B}$	(1/4)(1 – x)
B–B–B~B	$2\frac{n_B(n_B-1)}{n_A+n_B}$	(1/2)(1 – x)^2
B~A–A~B	$\frac{n_A n_B(n_B-1)}{(n_A+n_B)(n_A+n_B-1)}$	(1/4)x(1 – x)^2
A–A–A~B	$2\frac{n_A n_B}{n_A+n_B}$	(1/2)x(1 – x)
A~A–A~B	$2\frac{n_A(n_A-1)n_B}{(n_A+n_B)(n_A+n_B-1)}$	(1/2)x^2(1 – x)
A–A~B–B	$3\frac{n_A n_B}{n_A+n_B}$	(3/4)x(1– x)
A~B–B–B	$2\frac{n_A n_B}{n_A+n_B}$	(1/2)x(1 – x)
A–A~B	$3\frac{n_A n_B}{n_A+n_B}$	(3/4)x(1 – x)
A~B–B	$2\frac{n_A n_B}{n_A+n_B}$	(1/2)x(1 – x)

The geometrical factors of (5) and (6) are the sums of those listed in Table 1,

$$p_1^{(A\cdots A)} = p_1^{(A-A-A-A)} + p_1^{(A-A\sim A-A)} + p_1^{(A-A-A\sim A)} + p_1^{(A\sim A-A\sim A)} = \frac{x+4x^2+x^3}{4} \tag{32}$$

$$p_1^{(B\cdots B)} = p_1^{(B-B-B-B)} + p_1^{(B-B\sim B-B)} + p_1^{(B-B-B\sim B)} + p_1^{(B\sim A-A\sim B)} = \frac{x+6x+x^2+x^3}{4} \tag{33}$$

and

$$p_1^{(A\cdots B)} = p_1^{(A-A-A\sim B)} + p_1^{(A\sim A-A\sim B)} + p_1^{(A-A\sim B-B)} + p_1^{(A\sim B-B-B)} = \frac{7x-5x^2-2x^3}{4} \tag{34}$$

Because of the structural identity of the 1,2 and 1,4 PB monomers in both blend components, the calculation of the geometrical factors $p_2^{(C\cdots C)}$, $p_2^{(D\cdots D)}$, and $p_2^{(C\cdots D)}$ procceds exactly as in (32–34), where the individual coefficients $p_2^{(\text{chain pattern})}$ follow directly from $p_1^{(\text{chain pattern})}$ by substituting y for x in the third column of Table 1. Finally, the required combinations compress to

$$p_1 = p_1^{(A\cdots A)} + p_1^{(B\cdots B)} + p_1^{(A\cdots B)} = (4+2x)/4 \tag{35}$$

and

$$p_2 = p_2^{(C\cdots C)} + p_2^{(D\cdots D)} + p_2^{(C\cdots D)} = (4+2y)/4 \tag{36}$$

For completeness, Table 1 also summarizes the geometrical factors $N_1^{(2)}$(X–X~Y) and $r_1 \equiv N_1^{(2)}$(X–X~Y)/M_1 of (5) and (6). Similarly, $r_2^{(C-C\sim D)}$ and $r_2^{(C\sim D-D)}$ can be generated from $r_1^{(A-A\sim B)}$ and $r_1^{(A\sim B-B)}$ by substituting y for x in Table 1.

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