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Explanation for the Inversion of an UCST Phase Diagram to a LCST Diagram in Binary Polybutadiene Blends

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ABSTRACT: A simplified version of the random copolymer lattice cluster theory has been applied to explain the variation in the nature of the phase transition (upper vs lower critical solution temperature phase diagram) with the microstructure of isotopic polybutadiene (PB) blends that has been observed by Hashimoto and co-workers (*Macromolecules* **1992**, *25*, 6078). This variation occurs within our theory when the temperature-dependent portion χ_h of the effective interaction parameter χ_{SANS} becomes negative (due to an increasing difference $|y-x|$ in the compositions x and y of the two PB random copolymers) and competes with a positive temperature-independent, "entropic" portion χ_s of χ_{SANS}. The analysis is based on two important features. First is the calculation of χ_s solely from the monomer united atom molecular structures, with no adjustable parameters. Second is the treatment of the van der Waals interaction energies in terms of united atom groups.

Blends of perdeuterated (DPB) and protonated (HPB) polybutadienes have been the subject of extensive experimental investigations[1−4] as important examples of weakly interacting systems. Both blend components are typical random copolymers because of the presence of varying degrees of randomly placed 1,2- and 1,4-PB addition units along the polymer chain. These isotopic blends also exemplify the simplest types of A_xB_{1-x}/C_yD_{1-y} binary mixtures, i.e., mixtures of two chemically different random copolymers with different monomer compositions x and y.

Early studies by Bates et al.[1,2] and by Sakurai et al.[3] reveal that these systems exhibit an upper critical solution temperature (UCST), undergoing phase separation upon cooling. Subsequent work has been devoted to probe how the isotope effect and the blend microstructure combine to influence the miscibility patterns of these random copolymer binary mixtures. In particular, a series of systematic small-angle neutron-scattering experiments by Jinnai and co-workers[4] demonstrate that the prior observed UCST phase diagram converts remarkably to a lower critical solution temperature (LCST) diagram with an increase in the vinyl content of the HPB when the vinyl content of DPB remains fixed. This interesting phenomenon cannot be explained by the traditional extension[5,6] of FH theory to random copolymers since this theory is capable, at most, of predicting the conversion of an UCST phase behavior into to a phase diagram with complete miscibility. The FH random copolymer theory completely fails to explain the occurrence of a LCST phase diagram because the theory is derived under the assumption that the individual $\chi_{\alpha\beta}$ values are of purely energetic origin and, therefore, does not apply when the experimental effective parameters χ_{SANS} contain significant temperature independent portions.

The present paper applies a simplified "pedestrian" version[7] of the random copolymer lattice cluster theory (LCT) to these isotopic PB blends to elucidate the molecular factors responsible for the transition from UCST to LCST behavior with varying microstructure.

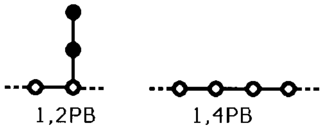

Figure 1. United atom structures for 1,2- and 1,4-polybutadiene (PB) monomers. Open circles denote united atom groups belonging to the chain backbone, while filled circles indicate the side groups.

This simplified random copolymer LCT has recently been used[7] to explain physical trends in the thermodynamics of random copolymer blends that cannot be described by prior random copolymer theories. The "pedestrian" version of the lattice cluster theory for random copolymers systems is based on two significant improvements beyond standard FH random copolymer theory.[7] First, the theory describes the polymer−polymer interactions in terms of the more realistic interactions between united atom groups [CH_n ($n = 1, 2$) groups for PB]. Figure 1 depicts the quite obvious united atom group models for the 1,2 and 1,4 addition monomers. There is no distinction between cis and trans 1,4 units, nor between head-to-head and head-to-tail[8] placements of successive 1,2 units although these fine details undoubtedly have a secondary influence on the blend compatability. Second, the theory provides an explicit equation (with no adjustable parameters) for the temperature-independent contribution χ_s to the effective interaction parameter χ. This "entropic" χ_s is formally absent from FH theory, but arises naturally[7] in the LCT, as a function of the compositions x and y of two random copolymers, from the different monomer structures of the 1,2- and 1,4-PB units (see Figure 1). The assumption of blend incompressibility is also employed for simplicity and to minimize the number of adjustable parameters required.

As discussed in ref 7, the small-angle neutron-scattering (SANS) effective monomer−monomer interaction χ parameter for A_xB_{1-x}/C_yD_{1-y} binary random copolymer blends is determined within the "pedestrian"

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LCT as

$$\chi_{\mathrm{SANS}} = c\left\{\frac{1}{z^2}(r_1 - r_2)^2 + \frac{1}{s_1 s_2}[\chi_{\mathrm{AC}} x y s_{\mathrm{A}} s_{\mathrm{C}} + \chi_{\mathrm{BC}}(1 - x) y s_{\mathrm{B}} s_{\mathrm{C}} + \chi_{\mathrm{AD}} x(1 - y) s_{\mathrm{A}} s_{\mathrm{D}} + \chi_{\mathrm{BD}}(1 - x)(1 - y) s_{\mathrm{B}} s_{\mathrm{D}} - \chi_{\mathrm{AB}} x(1 - x) s_{\mathrm{A}} s_{\mathrm{B}} s_2/s_1 - \chi_{\mathrm{CD}} y(1 - y) s_{\mathrm{C}} s_{\mathrm{D}} s_1/s_2]\right\} \quad (1)$$

where macroscopic interaction parameters $\{\chi_{\alpha\beta}\}$ between monomers of species α and β are expressed in terms of the nearest neighbor attractive van der Waals energies $\{\epsilon_{\alpha\beta}\}$

$$\chi_{\alpha\beta} = (z/2)(\epsilon_{\alpha\alpha} + \epsilon_{\beta\beta} - 2\epsilon_{\alpha\beta})/(kT) \quad (2)$$

with z the lattice coordination number (taken as $z = 6$ because the entropic part of eq 1 has been computed using a cubic lattice), k the Boltzmann constant, and T the absolute temperature. For simplicity, to keep the number of adjustable parameters to a bare minimum, all united atom groups of a given monomer are assumed to interact with the same monomer average van der Waals energy $\epsilon_{\alpha\beta}$. The entropic structural parameters r_1 and r_2 for the random copolymer blend components 1 and 2 are obtained[7] simply by counting the numbers of tri- ($s_\alpha^{(\mathrm{tri})}$) and tetrafunctional ($s_\alpha^{(\mathrm{tetr})}$) groups in the individual monomers of blend species α and by weighting these numbers by the corresponding compositions of the random copolymers. Since component 1 contains monomers of types A and B, while component 2 is composed of monomers of types C and D, the theory of ref 7 yields

$$r_1 = \frac{[s_{\mathrm{A}} + s_{\mathrm{A}}^{(\mathrm{tri})} + 3s_{\mathrm{A}}^{(\mathrm{tetr})}]x + [s_{\mathrm{B}} + s_{\mathrm{B}}^{(\mathrm{tri})} + 3s_{\mathrm{B}}^{(\mathrm{tetr})}](1 - x)}{s_{\mathrm{A}} x + s_{\mathrm{B}}(1 - x)} \quad (3)$$

$$r_2 = \frac{[s_{\mathrm{C}} + s_{\mathrm{C}}^{(\mathrm{tri})} + 3s_{\mathrm{C}}^{(\mathrm{tetr})}]y + [s_{\mathrm{D}} + s_{\mathrm{D}}^{(\mathrm{tri})} + 3s_{\mathrm{D}}^{(\mathrm{tetr})}](1 - y)}{s_{\mathrm{C}} y + s_{\mathrm{D}}(1 - y)} \quad (4)$$

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 or, equivalently, to the number of united atom groups in an α monomer. A conversion factor c in eq 1 rescales the LCT χ, which is computed as an united atom−united atom interaction parameter, to a monomer−monomer interaction parameter χ_{SANS} for comparison with experiment. As shown in the Appendix, c depends on the choice of the reference volume v_0 employed in the experimental data analysis. This c is a function of the averaged monomer site occupancy indices s_1 and s_2 that are defined for the $\mathrm{A}_x\mathrm{B}_{1-x}$ and $\mathrm{C}_y\mathrm{D}_{1-y}$ chains as

$$s_1 = s_{\mathrm{A}} x + s_{\mathrm{B}}\,(1 - x) \text{ and } s_2 = s_{\mathrm{C}} y + s_{\mathrm{D}}(1 - y) \quad (5)$$

respectively. At this stage, the theory is incapable of distinguishing random copolymers from block or alternating copolymers with the same compositions, but the theory does introduces a dependence on the monomer structures, a feature that is responsible for the presence of the temperature independent "entropic" contribution χ_s in χ_{SANS}. Ignoring the temperature independent contribution to χ and taking each monomer to occupy a single lattice site, i.e., setting $s_{\mathrm{A}} = s_{\mathrm{B}} = s_{\mathrm{C}} = s_{\mathrm{D}} = 1$ in eq 1, reduces the latter equation to the well-known random copolymer Flory−Huggins expression derived by ten Brinke et al.[5]

$$\chi_{\mathrm{FH}} = \chi_{\mathrm{AC}} xy + \chi_{\mathrm{BC}}(1 - x)y + \chi_{\mathrm{AD}} x(1 - y) + \chi_{\mathrm{BD}}(1 - x)(1 - y) - \chi_{\mathrm{AB}} x(1 - x) - \chi_{\mathrm{CD}} y(1 - y) \quad (6)$$

Let component 1 designate an $\mathrm{A}_x\mathrm{B}_{1-x}$ random copolymer with a fraction x of perdeuterated 1,2 units and a fraction $(1 - x)$ of perdeuterated 1,4 units (A ≡ D1,2 and B ≡ D1,4), whereas component 2 denotes a statistical copolymer $\mathrm{C}_y\mathrm{D}_{1-y}$ of hydrogenated 1,2 and 1,4 PB monomers (C ≡ H1,2 and D ≡ H1,4). Figure 1 depicts the obvious united atom monomer structures for both 1,2 and 1,4 monomers. Noticing from Figure 1 that the monomer structures for PB imply that $s_{\mathrm{A}} = s_{\mathrm{B}} = s_{\mathrm{C}} = s_{\mathrm{D}} = 4$, $s_{\mathrm{A}}^{(\mathrm{tri})} = s_{\mathrm{C}}^{(\mathrm{tri})} = 1$, $s_{\mathrm{B}}^{(\mathrm{tri})} = s_{\mathrm{D}}^{(\mathrm{tri})} = 0$, and $s_{\mathrm{A}}^{(\mathrm{tetr})} = s_{\mathrm{B}}^{(\mathrm{tetr})} = s_{\mathrm{C}}^{(\mathrm{tetr})} = s_{\mathrm{D}}^{(\mathrm{tetr})} = 0$, the partial entropic structural parameters r_1 and r_2 of eqs 3 and 4 and simplify to

$$r_1 = \frac{(4 + 1)x + 4(1 - x)}{4x + 4(1 - x)} = \frac{x + 4}{4} \quad (7)$$

and

$$r_2 = \frac{(4 + 1)y + 4(1 - y)}{4y + 4(1 - y)} = \frac{y + 4}{4} \quad (8)$$

while the average monomer site occupancy indices s_1 and s_2 of eq 5 are $s_1 = 4x + 4(1 - x) = 4$ and $s_2 = 4y + 4(1 - y) = 4$.

Our analysis of the experimental data[4] for isotopic PB blends is based on eq 1 and on another simplifying assumption that is designed to reduce further the number of adjustable parameters (i.e., the $\{\epsilon_{\alpha\beta}\}$) 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.[9]

$$\epsilon_{\mathrm{AA}} = \gamma^2\epsilon_{\mathrm{CC}}, \quad \epsilon_{\mathrm{BB}} = \gamma^2\epsilon_{\mathrm{DD}}, \quad \epsilon_{\mathrm{AB}} = \gamma^2\epsilon_{\mathrm{CD}} \quad (9)$$

$$\epsilon_{\mathrm{AC}} = \gamma\epsilon_{\mathrm{CC}}, \quad \epsilon_{\mathrm{BD}} = \gamma\epsilon_{\mathrm{DD}}, \quad \epsilon_{\mathrm{AD}} = \epsilon_{\mathrm{BC}} = \gamma\epsilon_{\mathrm{CD}} \quad (10)$$

where the scaling factor γ is less that unity to reflect the weaker attraction of the deuterated species. Again, to minimize the number of parameters, γ is taken as the same for the 1,2 and 1,4 units.

Given the above model, the small-angle neutron-scattering χ_{SANS} parameter of eq 1 is converted (see Appendix) to the rather compact result for the DPB/HPB blends

$$\chi_{\mathrm{SANS}} = \frac{2z}{kT}\{\epsilon_{\mathrm{CC}}(\gamma x - y)^2 + \epsilon_{\mathrm{DD}}[\gamma(1 - x) - (1 - y)]^2 - 2\epsilon_{\mathrm{CD}}[y - \gamma x][\gamma(1 - x) - (1 - y)]\} + \frac{1}{4z^2}[x - y]^2 \quad (11)$$

The expression for χ_{SANS} in eq 11 contains only four adjustable parameters: the polarizability scaling factor γ and the three microscopic van der Waals energies ϵ_{CC}, ϵ_{DD}, and ϵ_{CD} describing interactions between a pair of

Table 1. Comparison between Theory and Experiment for the Small Angle Neutron Scattering (SANS) Interaction Parameter $\chi_{SANS} = \chi_s + \chi_h/T$ of Isotopic DPB(x)/HPB(y) Poly(butadiene) Blends[a]

blend sample $\phi_{DPB} = 0.72$	$\chi_s \times 10^{-4}$ experiment	$\chi_s \times 10^{-4}$ theory	χ_h experiment	χ_h theory
DPB(16)/HPB(17)	−4.38	1.36×10^{-2}	0.352	0.784
DPB(16)/HPB(39)	−5.19	3.80	0.234	0.214
DPB(16)/HPB(52)	3.57	9.30	−0.144	−0.128
DPB(16)/HPB(65)	14.6	16.9	−0.556	−0.457
DPB(16)/HPB(80)	30.3	29.2	−0.814	−0.859

[a] The numbers in parentheses indicate the rounded off values for the percentage of 1,2 units in the random copolymers. Precise values are used for x and y from the first column in Table 1 of ref 4.

H1,2, a pair of H1,4, and between an H1,2 and H1,4 species, respectively. Using the standard representation of χ_{SANS}

$$\chi_{SANS} = \chi_s + \frac{\chi_h}{T} \tag{12}$$

the entropic and energetic contributions to χ_{SANS} of eq 11 emerge as

$$\chi_s = \frac{1}{4z^2}[x - y]^2 \tag{13}$$

and

$$\chi_h = \frac{2z}{k}\{\epsilon_{CC}(\gamma x - y)^2 + \epsilon_{DD}[\gamma(1 - x) - (1 - y)]^2 - 2\epsilon_{CD}[y - \gamma x][\gamma(1 - x) - (1 - y)]\} \tag{14}$$

The four parameters of eq 14 are fit to experimental data[4] for $\chi_{SANS}(T)$ from a series of five isotopic PB random copolymer blends with varying compositions y of the protonated PB species and a constant composition x of the deuterated polybutadiene. The temperature-independent part χ_s of χ_{SANS} follows directly from eq 13 with no adjustable parameters! The comparison of theory and experiment[4] is illustrated in Table 1 which summarizes values of both χ_s and χ_h for the five blends analyzed in the SANS experiments. The theory reproduces semiquantitatively the experimental SANS data of Jinnai[4] in the sense that it describes precisely the variation in the nature of the phase transition (upper vs lower critical solution temperature phase diagram) with the microstructure of isotopic PB blends. As shown in Table 1, the type of phase behavior is correctly predicted by the theory for all five PB blends considered. A LCST phase diagram for the isotopic PB blends arises within our theory from the competition between a negative energetic portion χ_h and a sufficiently positive entropic part χ_s of χ_{SANS}. Generally, the spinodal condition for a binary incompressible blend takes the form

$$\frac{1}{M_1\phi} + \frac{1}{M_2(1 - \phi)} - 2\left[\chi_s + \frac{\chi_h}{T}\right] = 0 \tag{15}$$

where ϕ is the blend composition and M_1 and M_2 are the numbers of united atom groups in the individual chains of species 1 and 2, respectively. When χ_h is negative, a sufficiently large $\chi_s > 0$ yields LCST phase behavior despite our assumption that the blend is incompressible.[10]

Except for one blend sample (where both x and y are low and very similar to each other), the experimental and theoretical values of χ_h accord reasonably well. Good agreement for the temperature independent portion χ_s of χ_{SANS} is limited, however, to the two samples with the largest compositional difference $\delta = |y - x|$ and the largest experimental χ_s. The experimental values of χ_s are negative for the blend samples with $\delta = 0.01$ and 0.23, but the simplified theory predicts χ_s as always positive. This feature precludes obtaining a perfect fit to the data. However, as discussed elsewhere,[10,11] more detailed LCT description can yield small negative χ_s of magnitudes comparable to those observed for two samples when the theory includes chain semiflexibility and/or blend compressibility. Another neglected feature that may affect χ_s is the presence of cis−trans randomness of the 1,4-butadiene units, a feature not easily modeled by a simple analytical approach. While the "pedestrian" random copolymer theory has just been extended[12] to provide nonrandom mixing, monomer sequence dependent contributions to the surface fractions, the cis−trans randomness in the experimental samples cannot be addressed even by this extended theory. The interaction energies ϵ_{CC}, ϵ_{DD}, and ϵ_{CD} and the polarizability factor γ are obtained as $\epsilon_{CC}/k \equiv \epsilon_{1,2-1,2}/k = 390.24$ K, $\epsilon_{DD}/k \equiv \epsilon_{1,4-1,4}/k = 406.85$ K, $\epsilon_{CD}/k \equiv \epsilon_{1,2-1,4}/k = 398.46$ K, and $\gamma = 0.987$. The value of γ is in line with the estimations of Bates et al.[9] indicating that γ lies in the range 0.98−0.99. (In fact, γ is constrained to lie in this range during the fitting process. Hence, γ is barely an adjustable parameter.) The differences between $\epsilon_{1,2-1,2}$, $\epsilon_{1,4-1,4}$, and $\epsilon_{1,2-1,4}$ are indeed small, as expected for weakly interacting systems. The fits are, however, not unique, and there are many sets of ϵ_{CC}, ϵ_{DD}, ϵ_{CD}, and γ that lead to similar accuracies in reproducing the SANS data[4] to those illustrated in Table 1. The value of the heterocontact interaction energy $\epsilon_{1,2-1,4}$ departs from that resulting from the Berthelot geometric combining rule[13] by the very small amount of about 0.02%. Note that fixing $\epsilon_{1,2-1,4}$ as the geometrical mean of the self-interaction energies $\epsilon_{1,2-1,2}$ and $\epsilon_{1,4-1,4}$ and not allowing $\epsilon_{1,2-1,4}$ to be an adjustable parameter automatically leads to a positive χ_h for arbitrary microstructures of the isotopic PB blends and, therefore, always to the prediction of an UCST phase behavior.

Using the above values for the γ and the three van der Waals energies ϵ_{CC}, ϵ_{DD}, and ϵ_{CD}, we find, in agreement with Sakurai et al.,[3] that the polybutadiene blends studied in ref 3 exhibit only an UCST phase diagram (both χ_s of eq 13 and χ_h of eq 14 are positive for these samples).

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Appendix: Relationship between the Experimental and the LCT SANS Interaction Parameters

The LCT effective interaction parameter χ_{site} is defined for an incompressible monodisperse binary blend as[10]

$$\chi_{\text{site}} = \frac{1}{2}\left[\frac{1}{M_1\phi} + \frac{1}{M_2(1-\phi)} - \frac{\partial^2\{f/kT\}}{\partial\phi^2}\bigg|_{V,T}\right] \quad \text{(A1)}$$

where M_1 and M_2 are the numbers of united atom groups in the individual chains of polymer species 1 and 2, f is the blend Helmholtz free energy (per united atom group), and $\phi \equiv \phi_1$ indicates the blend composition. On the other hand, the experimental SANS parameter χ_{SANS} of Jinnai et al.[4] has been determined using the representation

$$\chi_{\text{SANS}} = \frac{1}{2}v_0\left[\frac{1}{\langle N_1\rangle_{\text{w}}\phi v_1} + \frac{1}{\langle N_2\rangle_{\text{w}}(1-\phi)v_2} - \frac{k_{\text{N}}}{I(0)}\right] \quad \text{(A2)}$$

where $\langle N_1\rangle_{\text{w}}$ and v_i denote the weight-average degree of polymerization and the molar monomer volume of species i, respectively, $v_0 \equiv [\phi/v_1 + (1 - \phi)/v_2]^{-1}$ designates the arbitrarily chosen normalization volume, $I(0)$ is the extrapolated zero angle scattering intensity, and the scattering contrast factor $k_{\text{N}} = N_0(b_1/v_1 - b_2/v_2)^2$ is represented in terms of the monomer scattering lengths b_i, with N_0 being Avogadro's number. Besides the different normalizations of χ in eqs 1 and 2 (per united atom group for eq A1 vs per monomer for eq A2), there is another important difference between these two definitions. The expression A2 accounts for the polydispersity of the two blend components, whereas the definition A1 assumes a monodisperse binary blend. To ensure that the comparison between the experimental and theoretical interaction parameters is on an equal footing, we also have to redefine the theoretical χ for a polydisperse blend.

Consider a binary polymer blend containing n distinct polymers of species A with chain occupancy indices $\{M_{\text{A}}^{(i)} = N_{\text{A}}^{(i)}s_{\text{A}}\}$ and compositions $\{\phi_{\text{A}}^{(i)}\}$ ($i = 1, ..., n$) and m distinct polymers of species B with chain occupancy indices $\{M_{\text{B}}^{(j)} = N_{\text{B}}^{(j)}\, s_{\text{B}}\}$ and compositions $\{\phi_{\text{B}}^{(j)}\}$ ($j = 1, ..., m$). The differences among the n species of A type polymers and among the m species of B type polymers arise here only from the distributions in molecular weights (i.e., in the polymerization indices $\{N_{\text{A}}^{(i)}\}$ and $\{N_{\text{B}}^{(j)}\}$). The volume fractions $\phi_{\text{A}}^{(i)}$ and $\phi_{\text{B}}^{(j)}$ of the individual components satisfy conditions

$$\sum_{i=1}^{n} \phi_{\text{A}}^{(i)} = \phi_{\text{A}} \quad \text{(A3)}$$

and

$$\sum_{j=1}^{m} \phi_{\text{B}}^{(j)} = \phi_{\text{B}} \quad \text{(A4)}$$

where the overall compositions ϕ_{A} and ϕ_{B} of the components A and B, respectively, sum to unity

$$\phi_{\text{A}} + \phi_{\text{B}} = 1 \quad \text{(A5)}$$

Standard RPA theory[14] for a multicomponent incompressible system yields the zero angle partial structure factors $S_{\alpha\beta}^{(\text{poly})}(0)$ as

$$[\mathbf{S}^{(\text{poly})}(0)^{-1}]_{\alpha\beta} = \left[\frac{\delta_{\alpha\beta}}{M_\alpha\phi_\alpha}\right] + 2\,\chi_{\alpha\beta} \quad \text{(A6)}$$

where the subscripts $\alpha = 1, 2, ..., n + m$ and $\beta = 1, 2, ..., n + m$ label all polymer species, $\delta_{\alpha\beta}$ denotes the Kronecker δ function, $\chi_{\alpha\beta}$ designates the macroscopic interaction parameter between α–β monomer pairs, and $M_\alpha = N_\alpha s_\alpha$ is a product of the polymerization index N_α of species α and the monomer α site occupancy index s_α. Equation A6 is presented in matrix notation for the specific $q = 0$ limit.

The description of a polydisperse A/B binary blend with eq A6 only requires the specification of the three interaction parameters χ_{AA}, χ_{BB}, and χ_{AB} and the polymerization indices $\{M_\alpha\}$. Under the assumption that only the monomers from one type of polymers, say polymers A, scatter the neutrons, the expression for the overall scattering intensity $I(0)$ becomes proportional to $S^{(\text{poly})}(0)$, which is a simple sum of the partial structure factors $S_{ii'}^{(\text{poly})}$ for all chains of species A

$$S^{(\text{poly})}(0) = S_{\text{AA}}^{(\text{poly})}(0) = \sum_{i,i'}^{n} S_{ii'}^{(\text{poly})}(0) \quad \text{(A7)}$$

The partial structure factors $S_{\alpha\beta}^{(\text{poly})}(0)$ of eq A7 are evaluated by inversion of the $(n + m) \times (n + m)$ matrix $\mathbf{S}^{(\text{poly})}(0)^{-1}$ from eq A6. The effective interaction parameter $\chi_{\text{site}}^{(\text{poly})}$ for an incompressible polydisperse binary blend is defined in terms of the total zero angle scattering $S^{(\text{poly})}(0)$ of eq A7 by the standard RPA formula[14,15]

$$\chi_{\text{site}}^{(\text{poly})} = \frac{1}{2}\left[\frac{1}{\langle M_{\text{A}}\rangle_{\text{w}}\,\phi} + \frac{1}{\langle M_{\text{B}}\rangle_{\text{w}}\,(1-\phi)} - \frac{1}{S^{(\text{poly})}(0)}\right] \quad \text{(A8)}$$

where $\langle M_{\text{A}}\rangle_{\text{w}} = \langle M_{\text{A}}{}^2\rangle/\langle M_{\text{A}}\rangle$ and $\langle M_{\text{B}}\rangle_{\text{w}} = \langle M_{\text{B}}{}^2\rangle/\langle M_{\text{B}}\rangle$ are the weight-average degrees of polymerization.

Within the simple model in which the LCT χ_{site} is independent of molecular weights, detailed analysis of eqs A1 and A6–A8 (through several numerical examples[16] with $n = m = 101$) leads to identity

$$\chi_{\text{site}} = \chi_{\text{site}}^{(\text{poly})} \quad \text{(A9)}$$

independent of whether M_1 and M_2 of eq A1 are taken as $\langle M_1\rangle_{\text{w}}$ and $\langle M_2\rangle_{\text{w}}$, respectively, or as $\langle M_1\rangle_n \equiv \langle M_1\rangle$ and $\langle M_2\rangle_n \equiv \langle M_2\rangle$ (provided the same molecular weights are employed in the free energy expression). The insensitivity of eq A9 to the choice of M_1 and M_2 arises from the assumed blend incompressibility and from the assumed independence of χ_{site} on molecular weights. Thus, establishing the relation between the experimental and LCT interaction parameters of eqs A2 and A8 requires only reexpressing $\chi_{\text{site}}^{(\text{poly})}$ as a monomer–monomer interaction parameter.

In the limit of an incompressible blend, the LCT scattering intensity $I(0)$ becomes[10,17] a function of only one scattering factor [e.g., $S_{11}^{(\text{poly})}(0)$]

$$I(0) = S_{11}^{(\text{poly})}(0)\left[\frac{b_1}{s_1} - \frac{b_2}{s_2}\right]^2 \frac{1}{v_{\text{cell}}} \quad \text{(A10)}$$

where s_i designates the number of lattice sites occupied by a single monomer of species i and $v_{\text{cell}} = V/N_l$ is the volume associated with a single lattice site. Given the assumption of blend incompressibility, the unit volume v_{cell} of a blend is approximated by the geometrical mean of the unit volumes $v_1/(N_0s_1)$ and $v_2/(N_0s_2)$ of the pure blend components

$$v_{\text{cell}} = \left[\left(\frac{v_1}{N_0 s_1}\right)\left(\frac{v_2}{N_0 s_2}\right)\right]^{1/2} \tag{A11}$$

Substituting eqs A10 and A11 into eq A2 converts the latter to the form

$$\chi_{\text{SANS}} = \frac{1}{2} v_0 \left[\frac{1}{\langle N_1\rangle_{\text{w}}\, \phi v_1} + \frac{1}{\langle N_2\rangle_{\text{w}}\, (1-\phi) v_2} - \frac{(v_1 v_2)^{1/2}[b_1/v_1 - b_2/v_2]^2}{(s_1 s_2)^{1/2}[b_1/s_1 - b_2/s_2]^2 S_{11}^{(\text{poly})}(0)}\right] \tag{A12}$$

Assuming perfect contrast ($b_2 = 0$) reduces eq A12 to

$$\chi_{\text{SANS}} = \frac{1}{2} v_0 \left[\frac{1}{\langle N_1\rangle_{\text{w}}\, \phi v_1} + \frac{1}{\langle N_2\rangle_{\text{w}}\, (1-\phi) v_2} - \frac{s_1^{3/2}\, v_2^{1/2}}{s_2^{1/2}\, v_1^{3/2}} \frac{1}{S_{11}^{(\text{poly})}(0)}\right] \tag{A13}$$

Combining eqs A13 and A7−A9 enables relating the LCT interaction parameter χ_{site} to the experimental χ_{SANS} through

$$\chi_{\text{SANS}} = \frac{v_0}{2} \left[\frac{1}{\langle N_1\rangle_{\text{w}}\, \phi v_1} + \frac{1}{\langle N_2\rangle_{\text{w}}\, (1-\phi) v_2} - \frac{s_1^{3/2}\, v_2^{1/2}}{s_2^{1/2}\, v_1^{3/2}} \left(\frac{1}{\langle N_1\rangle_{\text{w}}\, s_1 \phi} + \frac{1}{\langle N_2\rangle_{\text{w}}\, s_2(1-\phi)} - 2\chi_{\text{site}}\right)\right] \tag{A14}$$

where the relation $\langle M_i\rangle_{\text{w}} = \langle N_i\rangle_{\text{w}} s_i$ is employed. After some simple algebra, eq A14 becomes transformed into the more convenient form

$$\chi_{\text{SANS}} = \frac{v_0}{2} \left\{\frac{1}{\langle N_1\rangle_{\text{w}}\, \phi}\left[\frac{1}{v_1} - \frac{s_1^{1/2}\, v_2^{1/2}}{s_2^{1/2}\, v_1^{3/2}}\right] + \frac{1}{\langle N_2\rangle_{\text{w}}\, (1-\phi)}\left[\frac{1}{v_2} - \frac{s_1^{3/2}\, v_2^{1/2}}{s_2^{3/2}\, v_1^{3/2}}\right] + 2\frac{s_1^{3/2}\, v_2^{1/2}}{s_2^{1/2}\, v_1^{3/2}} \chi_{\text{site}}\right\} \tag{A15}$$

Choosing the ratio of monomer site occupancy indices (s_1/s_2) to coincide with the ratio (v_1/v_2) of monomer molecular volumes makes the first two terms in the square brackets of eq A15 vanish identically, yielding the final scaling between the experimental χ_{SANS} of Jinnai et al.[4] and the incompressible model LCT interaction parameter χ_{site} of eq A1 as

$$\chi_{\text{SANS}} = \left[\frac{s_1 s_2}{s_1(1-\phi) + s_2\phi}\right] \chi_{\text{site}} \tag{A16}$$

The factor $s_1 s_2/[s_1(1-\phi) + s_2\phi]$ of eq A16 arises from the defintion by Jinnai et al.[4] of the reference volume as $v_0 = [\phi/v_1 + (1-\phi)/v_2]^{-1}$ and deviates from the factor $(s_1 s_2)^{1/2}$ derived by us in ref 10 when choosing $v_0 = (v_1 v_2)^{1/2}$ as the arbitrary reference volume. When $s_1 = s_2 = s$, both factors become identical and eq A16 simplifies to

$$\chi_{\text{SANS}} = s\chi_{\text{site}} \tag{A17}$$

References and Notes

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