Repeat-Unit Interaction Energies for Lattice Cluster Theory Derived from SANS Data for Blends of Random Poly(ethylene-butene-1)

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ABSTRACT: The SANS data for binary random poly(ethylene-butene-1) blends are analyzed using the lattice cluster theory (LCT) which relates bulk polymer properties to repeat-unit structures. The random poly(ethylene-butene-1) chains are approximated as monodisperse homopolymers. LCT repeat-unit interaction energies ϵ, ϵ_{11}, and ϵ_{22} are fitted to the Flory χ parameters obtained from the SANS experiments. The calculated χ parameters have the correct temperature dependence, and the predicted UCST's agree with the experimental data.

I. Introduction

Understanding the microstructure and phase behavior relationship for polymer blends and solutions is important from both technological and theoretical points of view. A common denominator of most thermodynamic theories and experimental approaches to understanding the phase behavior is an interaction parameter proposed by Flory[1] and often referred to as the χ parameter. In principle, the χ parameter should depend only upon temperature and account for the phase behavior of polymer blends. In paractice, χ is often found to depend also on composition, polydispersity, and molecular weight. Despite these flaws, the χ parameter gained wide acceptance as a universal tool for describing polymeric blends and solutions because it provides a simple and hence useful link between differential theoretical, e.g., refs 2 and 3, and experimental, e.g., small-angle neutron scattering (SANS),[4] approaches.

For example, Balsara et al.[5] determined χ from SANS data for a series of well-characterized blends of nearly monodisperse, random poly(ethylene-butene-1) (PEB, for short). They correlated their data within the framework of the Flory-Huggins theory and random-phase approximation (RPA) of de Gennes,[6] approximating the real random copolymer chains as model homopolymers. In the Flory-Huggins theory, the expression for the Gibbs energy of mixing for a binary homopolymer blend is

$$\frac{\Delta G_v}{k_B T} = \frac{\phi_1 \ln \phi_1}{v_1 N_1} + \frac{\phi_2 \ln \phi_2}{v_2 N_2} + \chi \frac{\phi_1 \phi_2}{v} \quad (1)$$

where ΔG_v is the Gibbs energy of mixing per unit volume, k_B is Boltzmann's constant, T is the absolute temperature, ϕ_1 and ϕ_2 are volume fractions of components 1 and 2, respectively, N_1 and N_2 are the corresponding degrees of polymerization, i.e., number of repeat-units per chain, v_1 and v_2 are the volumes of repeat units, v is the reference volume (usually $v = (v_1 v_2)^{1/2}$, but in general v can be arbitrary), and χ is the Flory interaction parameter. If $v = v_1 = v_2$, then the Gibbs energy per lattice site, ΔG_l, can be expressed as

$$\frac{\Delta G_l}{k_B T} = \frac{\phi_1 \ln \phi_1}{N_1} + \frac{\phi_2 \ln \phi_2}{N_2} + \chi \phi_1 \phi_2 \quad (2)$$

The Flory-Huggins theory can correctly predict the immiscibility of large polymers (due to small entropy of mixing) and the existence of the upper critical solution temperature (UCST) but fails to account for the lower critical solution temperature (LCST). The Flory equation of state[7-9] (based on an approach originated by Prigogine[10]) and its extensions due to Sanchez and Lacombe,[11,12] on the other hand, can account for LCST by introducing a concept of unoccupied lattice sites ("voids").

The Flory interaction parameter χ can be related to experimental data;[13] for example, it can be derived from a SANS static structure factor in the long-wavelength limit, $S_v(0)$, given as

$$\frac{1}{S_v(0)} = \frac{1}{v_1 \phi_1 N_1} + \frac{1}{v_2 \phi_2 N_2} - \frac{2\chi}{v} \quad (3)$$

Equation 3 can be derived either from eq 1, by taking the second derivative of $\Delta G_v / k_B T$ with respect to either volume fraction, or from RPA.

The objective of this work is to understand the microscopic origins of the χ parameter, by applying a newly developed lattice cluster theory (LCT) of Dudowicz and Freed,[14-18] to the set of experimental SANS data of Balsara et al.[5] We find LCT attractive because it explicitly accounts for repeat-unit structure effects on χ.

We briefly discuss LCT and our approximations needed to apply LCT to random copolymers. Analysis of our application of LCT and discussion of the results are given in section III.

II. Application of Lattice Cluster Theory to Random Copolymer Blends

Description of LCT. LCT allows for predicting thermodynamic properties of polymer blends in the state of phase equilibrium. The basis for LCT is a cubic lattice with N_l lattice sites. The LCT entropy of mixing is related to the number of ways a system of polymers can be placed into the lattice. Dudowicz and Freed derived the entropy and energy of mixing from a cluster expansion for multicomponent, and hence polydisperse, blends[16] and for binary blends.[17,18]

For example, the Helmholtz energy of mixing per lattice site, ΔA_l, for a binary blend is

$$\frac{\Delta A_l}{k_B T} = \phi_v \ln \phi_v + \frac{\phi_1}{M_1} \ln \phi_1 + \frac{\phi_2}{M_2} \ln \phi_2 + g_{12} \phi_1 \phi_2 + g_{1v} \phi_1 \phi_v + g_{2v} \phi_2 \phi_v \quad (4)$$

where M_1 and M_2 are site occupancies (numbers of occupied lattice sites) of polymers 1 and 2, respectively, and ϕ_1 and

Table I
Properties of Random PEB[5]

polymer[a]	no. of D atoms per C_4 repeat unit	no. of C_4 repeat units[b]	no. of ethyl branches per 100 backbone carbons	hypothetical homopolymer structure[c]
H78	0	1290	32	1b
H88	0	1610	39	1c
H97a	0	1600	47	1a
H97b	0	865	47	1a
D78	2.37	1290	32	1b
D88	2.96	1610	39	1c
D97a	2.79	1600	47	1a
D97b	2.69	865	47	1a

[a] H means hydrogenated, D means deuterated, and the number means mole percentage of 1,2 units (vinyl units) in precursor polybutadiene. [b] Estimated for hydrogenous samples by dividing the weight-average molecular weight (56.11), assumed to be the same for the deuterated samples. [c] Shown in Figure 1.

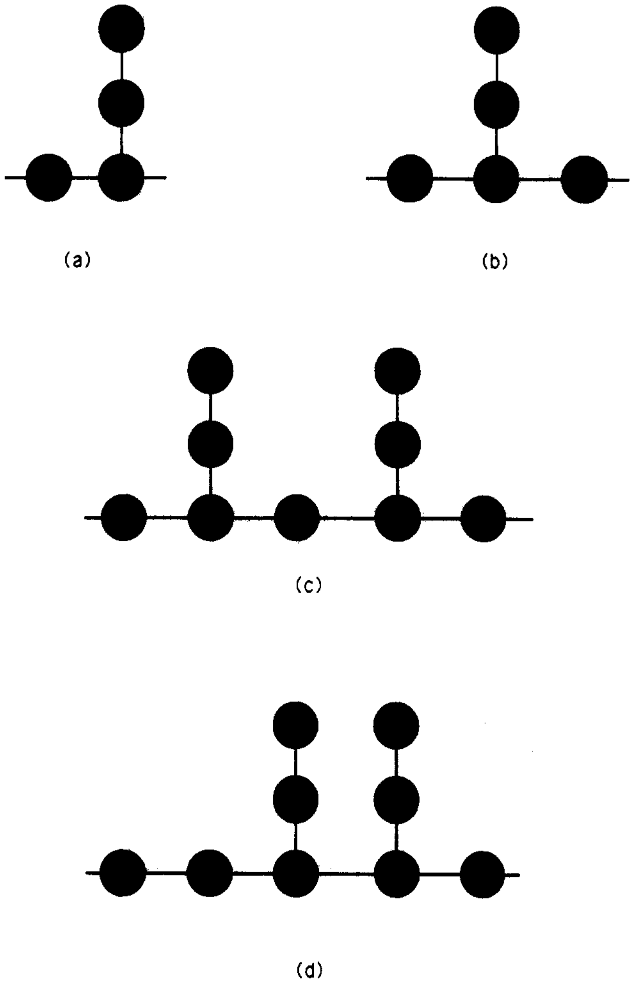

Figure 1. Model repeat-unit structures for three random copolymer blend components: (a) H97a (D97a) or H97b (D97b); (b) H78 (D78); (c and d) H88 (D88).

ϕ_2 are the corresponding volume fractions, defined as

$$\phi_1 = n_1/N_l \tag{5}$$

$$\phi_2 = n_2/N_l \tag{6}$$

where n_1 and n_2 are the number of lattice sites occupied by polymers 1 and 2, respectively, and N_l is the total number of lattice sites. Similarly, ϕ_ν is defined as

$$\phi_\nu = n_\nu/N_l \tag{7}$$

where n_ν is the number of empty lattice sites ("voids"). The g's of eq 4 are polynomials in the interaction energies ϵ, ϵ_{11}, and ϵ_{22} (where $\epsilon = \epsilon_{11} + \epsilon_{22} - 2\epsilon_{12}$), the inverse of the coordination number, z^{-1} ($z = 6$ in this work), and volume fractions ϕ_1, ϕ_2, and ϕ_ν. Each of the g's can be symbolically written as[18]

$$\sum_{m_\delta, m_\gamma, p, q} C^{(pq)}_{m_\delta, m_\gamma} {\phi_\delta}^{m_\delta} {\phi_\gamma}^{m_\gamma} z^{-p} {\epsilon_{\delta\gamma}}^{q} \tag{8}$$

where the coefficients $C^{(pq)}_{m_\delta, m_\gamma}$ depend exclusively and explicitly on the geometry of the repeat-unit. In order to determine the C's up to the second order in both ϵ's and z^{-1}, one has to calculate the geometric factors (counting indices) for repeat units of polymers 1 and 2, involving up to three bonds. For a given repeat-unit structure, these include $\mathcal{N}_1$, $\mathcal{N}_2$, $\mathcal{N}_3$, $\mathcal{N}_\perp$, $\mathcal{N}_{1,1}$, and $\mathcal{N}_{1,2}$, where $\mathcal{N}_i$ is the number of ways of selecting sequential sets of i bonds (i = 1, 2 or 3), $\mathcal{N}_\perp$ is the number of ways three bonds meet, and $\mathcal{N}_{1,1}$ and $\mathcal{N}_{1,2}$ can be expressed in terms of $\mathcal{N}_1$, $\mathcal{N}_2$, $\mathcal{N}_3$, and $\mathcal{N}_\perp$:[19]

$$2\mathcal{N}_{1,1} = {\mathcal{N}_1}^2 - \mathcal{N}_1 - 2\mathcal{N}_2 \tag{9}$$

$$\mathcal{N}_{1,2} = \mathcal{N}_1\mathcal{N}_2 - 2\mathcal{N}_2 - 2\mathcal{N}_3 - 3\mathcal{N}_\perp \tag{10}$$

Therefore, at this level of approximation, in order to determine ΔA_l as a function of ϕ_1, ϕ_2, ϕ_ν, M_1, M_2, ϵ's, and T, one needs to know only $\mathcal{N}_1$, $\mathcal{N}_2$, $\mathcal{N}_3$, and $\mathcal{N}_\perp$, for both, i.e., 1 and 2, repeat-unit structures.

The Gibbs energy of mixing can be calculated numerically from the Helmholtz energy of mixing by using the equation

$$\Delta G_l = \Delta A_l + P\Delta V_l \tag{11}$$

where ΔV_l is the volume of mixing per lattice site and P is pressure (P = 1 atm, in this work). This volume of mixing is equal to the net change of volume upon mixing, as defined in ref 18, divided by the total number of lattice sites. It can be derived[18] from the equation

$$P = -\frac{1}{v}\frac{\partial \Delta A_l}{\partial n_\nu}\Big|_{T,n_1,n_1} \tag{12}$$

which relates P and the number of voids for both the blend and the individual pure components. From ΔG_l, using the standard procedure,[18] one can calculate the spinodal curve for the binary blend. One can also, as later described, derive the χ parameter from ΔG_l. Similarly, as for ΔA_l, one needs to know only $\mathcal{N}_1$, $\mathcal{N}_2$, $\mathcal{N}_3$, and $\mathcal{N}_\perp$, for both repeat-unit structures, in order to be able to calculate ΔG_l, χ, and the spinodal curve as a function of ϕ_1, ϕ_2, M_1, M_2, ϵ's, P, and T.

PEB Repeat Unit Structure. PEB blend components have similar chemical character but differ in average

Table II
Geometrical Factors for Different Structures[a]

structure	$\mathcal{N}_1$	$\mathcal{N}_2$	$\mathcal{N}_3$	$\mathcal{N}_\perp$
Figure 1a	$2\mathcal{N}$	$(5/2)\mathcal{N} - 1$	$3\mathcal{N} - 4$	$(1/2)\mathcal{N}$
Figure 1b	$(5/3)\mathcal{N}$	$2\mathcal{N} - 1$	$(7/3)\mathcal{N} - 3$	$(1/3)\mathcal{N}$
Figure 1c	$(1/5)\ (9\mathcal{N} + 4)$	$(1/5)(11\mathcal{N} + 1)$	$(1/5)(13\mathcal{N} - 12)$	$(2/5)(\mathcal{N} + 1)$
Figure 1d	$(1/5)(9\mathcal{N} + 4)$	$(1/5)(11\mathcal{N} + 1)$	$(1/5)(14\mathcal{N} - 11)$	$(2/5)(\mathcal{N} + 1)$

[a] $\mathcal{N}$ is the number of bonds in the chain backbone.

Table III
LCT Interaction Energies ϵ for Different Blends[a]

blend	$\epsilon \times 10^4$	ϵ_{11}	ϵ_{22}
D78/H88	1.553	0.544	0.545
D88/H78	1.914	0.536	0.538
D88/H97a	1.296	0.536	0.536
D88/H97b	1.187	0.536	0.536
D97a/H88	1.268	0.545	0.545

[a] ϵ_{11} corresponds to the deuterated copolymer.

repeat-unit structure (geometry) and deuteration. PEB's are random copolymers that were synthesized as hydrogenated or deuterated polybutadiene by Balsara et al.[5] Therefore, these PEB's consist of two kinds of C_4 units: vinyl (two backbone carbons with an ethyl side branch, a result of 1,2 substitution) and butyl (four backbone carbons, a result of 1,4 substitution).

Balsara et al.[5] obtained three different microstructures, with 32, 39, and 47 ethyl branches (each 1,2 monomer gives rise to one branch per two backbone carbons while 1,4 monomer does not give branches at all) per 100 backbone carbons, and denoted H78, H88, and H97, respectively. The microstructure H97 appeared in two versions, H97a and H97b, differing in molecular weight. To provide the scattering contrast, the polymers were partially deuterated, resulting in corresponding components D78, D88, D97a, and D97b. Experimental characterization of the polymers studied in this work is summarized in Table I.

The critical step in applying LCT to these PEB's is the approximation of a random copolymer by an effective homopolymer, having the same branching density. This is most likely adequate for long-wavelength properties, but it might cause discrepancies for short-wavelength correlation between repeat-units.

In order to calculate the Gibbs energy in LCT, we need to know the repeat-unit structures which can further be used to determine the geometrical factors. The components H97a (D97) and H97b (D97b), which have 47 ethyl branches per 100 backbone carbons, are modeled as effective homopolymers whose repeat-unit structure is shown in Figure 1a. This structure has two backbone carbons and one branch with two carbons. Hence, it occupies four lattice sites. The geometrical factors for this repeat unit are reported in ref 18. The component H78 (D78) is modeled as an effective homopolymer whose repeat-unit structure is shown in Figure 1b. This repeat-unit has three backbone carbons and one branch. The component H88 (D88) is modeled as an effective homopolymer with the repeat-unit shown in Figure 1c. An alternative representation of this repeat-unit is shown in Figure 1d, where the ethyl branches are adjacent. In real random copolymers, due to the steric repulsions, the adjacent branches are very unlikely to appear. Therefore, we expect Figure 1c to be a more realistic representation of the real random copolymer than Figure 1d. The geometrical factors for structures presented in Figure 1 are shown in Table II.

Renormalizing the χ Parameter. As described in ref 5, the experimental χ parameter is calculated from eq 3 using a structure factor, obtained from the coherent scattering intensity, in the long-wavelength limit, $S_v(0)$. The χ parameter is always defined per reference volume (v), i.e., χ/v is invariant with respect to changes in v. In order to be able to relate the experimental and theoretical χ's, one needs to use the same reference volume. The χ parameter reported in ref 5 was calculated per reference volume which corresponds to the volume of a C_4 unit estimated as

$$v = (v_H v_D)^{1/2} \tag{13}$$

where v_H is the volume occupied by C_4H_8 unit, v_D is the volume occupied by the deuterated unit $C_4H_{8-n_D}D_{n_D}$, and n_D is an average number of deuterium atoms per C_4 unit.

In LCT, on the other hand, v_i is the volume of s_i lattice sites occupied by a repeat unit of polymer of type i, where $i = 1$ or 2. In our case s_i can be 4, 5, or 9, and the lattice constant is a. Therefore, $v_1 = s_1a^3$ and $v_2 = s_2a^3$, while the corresponding reference volume, v, is equal to $(s_1s_2)^{1/2}a^3$. This volume does not vary with temperature because, in this work, we use a version of the Dudowicz–Freed theory which does not allow for lattice constant variations with temperature. The actual, experimental reference volume can vary up to 10% due to thermal expansion.

The structure factor in the long-wavelength limit, $S_l(0)$, calculated from ΔG_l is given[17] as

$$S_l(0) = p_1^2S_{l,11}(0) + p_2^2S_{l,22}(0) + 2p_1p_2S_{l,12}(0) \tag{14}$$

where $S_{l,11}(0)$, $S_{l,22}(0)$, and $S_{l,12}(0)$ are the partial structure factors, defined in ref 17, and p_1 and p_2 are the normalized coherent scattering amplitudes (depending on n_D), which for the blends of this study we evaluate numerically as

$$p_2 = -0.319/n_D \tag{15}$$

$$p_1 = p_2 + 1 \tag{16}$$

In order to calculate χ from eq 3, we use the following straightforward identities:

$$a^3(s_1,s_2)^{1/2} = v \tag{17}$$

$$a^3M_1 = v_1N_1 = a^3s_1N_1 \tag{18}$$

$$a^3M_2 = v_2N_2 = a^3s_2N_2 \tag{19}$$

$$a^3S_l(0) = S_v(0) \tag{20}$$

Next, we renormalize the experimental χ's that have been calculated per volume of C_4 repeat unit which corresponds to $v = 4a^3$ in LCT. This way, the experimental and LCT values of χ correspond to each other.

III. Results and Discussion

We have experimental data for five random copolymer blends:[5] D78/H88, D88/H78, D88/H97a, D88/H97b, and D97a/H88. The interaction energies (ϵ, ϵ_{11}, and ϵ_{22}) for these blends are determined by least-squares regression of the χ experimental data. Initially, we regressed the

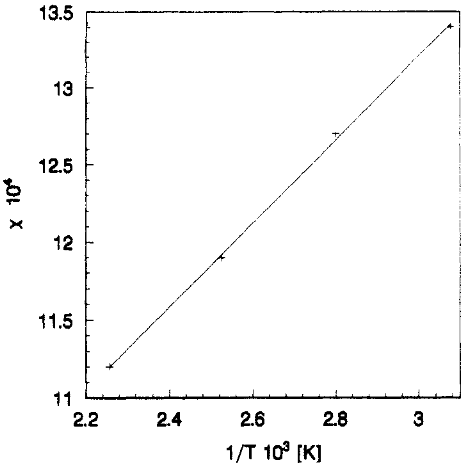

Figure 2. Comparison between experimental (+) and calculated (solid line) values of the χ interaction parameter plotted against the inverse temperature for a D88/H78 blend.

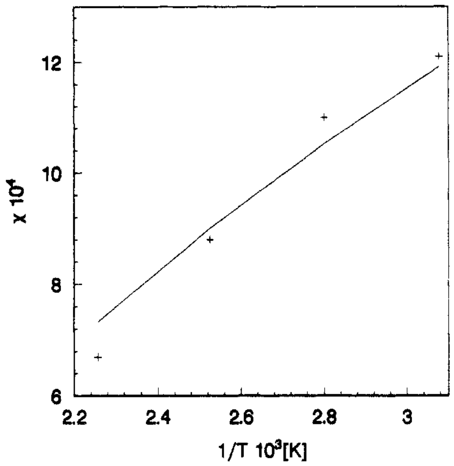

Figure 3. Comparison between experimental (+) and calculated (solid line) values of the χ interaction parameter plotted against the inverse temperature for a D97a/H88 blend.

experimental data for each blend separately and, hence, obtained ϵ_{11} and ϵ_{22} values that were different for the same polymer in different blends, for example, for H88 in blends with D78 and D97a. However, we also found that, while the χ parameter is rather sensitive to changes in ϵ, it is much less sensitive to changes in ϵ_{11} and ϵ_{22}. Therefore, we divide the experimental data for the five blends into two sets, (1) D78/H88 and D97a/H88 and (2) D88/H78, D88/H97a, and D88/H97b, which do not have common polymers, and regress each set separately. This way, we obtained unique and consistent values of ϵ, ϵ_{11}, and ϵ_{22} which are reported in Table III. Table III reports the results using the structure in Figure 1c for H88 (D88). The results for the structure in Figure 1d are very close, which suggests that such a small difference in repeat-unit structure has an insignificant effect on χ.

By contrast, the temperature has a significant effect on χ. The interaction parameter χ is plotted versus the inverse temperature, Figures 2–7, where curves are calculated from LCT, using interaction energies from Table III, while the points are the experimental χ's. The volume fraction of the deuterated component is denoted by ϕ.

In Figure 2 we show the calculated (LCT) and experimental χ for the D88/H78 blend ($\phi = 0.5$). For this blend the χ parameter is found to be nearly linearly dependent on inverse temperature:

$$\chi = A + B/T \tag{21}$$

where parameter A is referred to as an entropic contribution to χ, while B/T is referred to as an enthalpic contribution to χ.

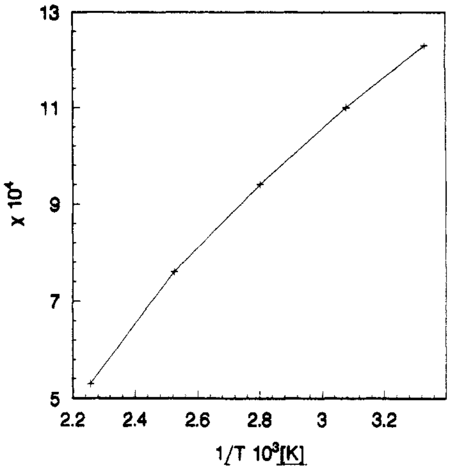

Figure 4. Comparison between experimental (+) and calculated (solid line) values of the χ interaction parameter plotted against the inverse temperature for a D88/H97b blend.

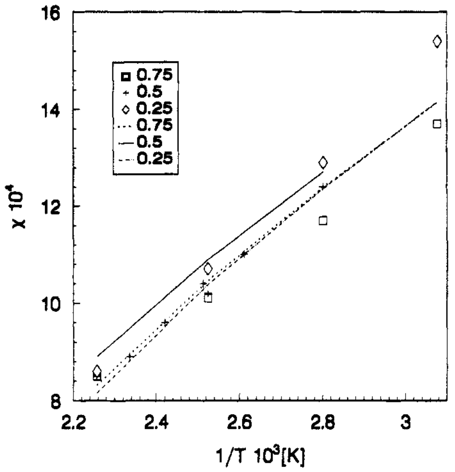

Figure 5. Comparison between experimental (◇, +, □) and calculated (dotted and solid lines) values of the χ interaction parameter plotted against the inverse temperature for a D78/H88 blend at three different compositions, as indicated.

In Figures 3 and 4 we present the data for the D97a/H88 and D88/H97b blends, respectively. The linear relationship does not reflect the observed curvature. LCT, on the other hand, especially in Figure 4, captures the observed curvature. All of the blend data discussed to this point have been at a single composition ($\phi = 0.5$).

We now consider the compositional effect. In Figure 5 we show χ plotted as a function of inverse temperature for the D78/H88 blend at three compositions. We note that the calculated composition effect does not match the experimental composition effect. For example, the experimental χ's decrease, at a given temperature, as the volume fraction of D78 increases, whereas, according to the LCT, there is a maximum in χ at a volume fraction of 0.5. However, we should also note that the estimated maximum uncertainty of the experimental χ is around 12%, and the composition-induced changes in χ are in this range.

In Figure 6 we show that χ exhibits a flat maximum when plotted versus ϕ at 84 °C for this blend. There is a very weak composition dependence in the range 0.25–0.75 which may not be experimentally detectable due to the 12% experimental uncertainty. However, at the extremes of composition, this effect should be measurable.

In this study, LCT is found to predict consistently that χ has a maximum at $\phi = 0.50$, but Dudowicz and Freed[17,18]

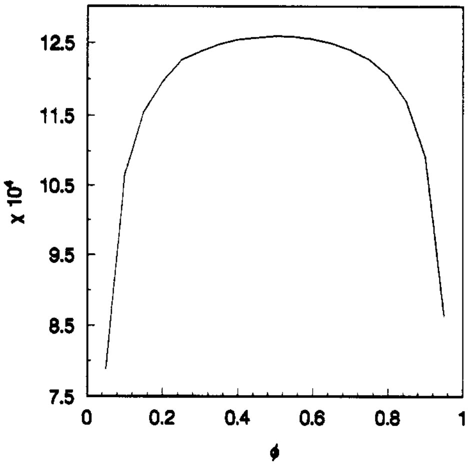

Figure 6. Calculated compositional dependence of χ for a D78/H88 blend at 84 °C. The calculations were based on data from a single composition, $\phi = 0.5$.

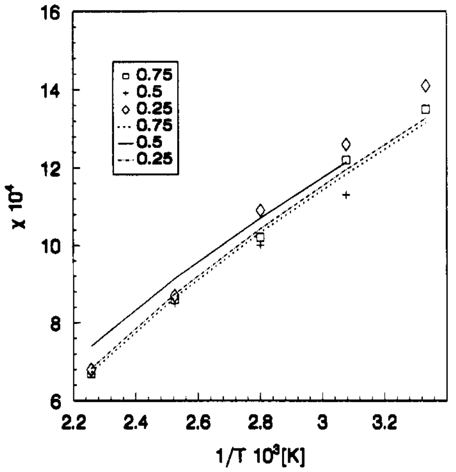

Figure 7. Comparison between experimental (◇, +, □) and calculated (dotted and solid lines) values of the χ interaction parameter plotted against the inverse temperature for a D88/H97a blend at three different compositions, as indicated.

demonstrated a variety of different functional dependencies for other systems. Also Bates et al.[4] found experimentally, for a different system, that χ has a minimum at $\phi = 0.50$ and accounted for this behavior using Muthukumar's fluctuation theory.[2]

In Figure 7 we show the data for the D88/D97a blend at three compositions, $\phi = 0.25$, 0.50, and 0.75. Again, within the 12% uncertainty range, the experimental data should not be interpreted as indicating a composition dependence. LCT predicts a maximum, similar to that seen for D78/H88.

In addition to being able to fit the experimental χ data, we are also able to determine the critical temperature. In Table IV we present the critical temperatures, of the UCST type, for all the blends in this study, determined from LCT using the interaction energies reported in Table III. There are no accurate experimental data with which to compare these calculations. However, Balsara et al.[5] observed UCST transitions: for D88/H97a and D97a/H88 (at 0.5 volume fraction) somewhere between 27 and 52 °C and for D78/H88 between 52 and 84 °C. The calculated critical temperatures are consistent with these observations, as are Balsara et al.'s[5] UCST estimates obtained from the Flory–Huggins theory. It is reassuring to find that the critical temperature predicted for the smaller polymer (H97b) is much lower than that for the larger polymer (H97a), as expected.

Table IV
Critical Temperatures (UCST) for Different Blends

blend	critical temp (°C)	blend	critical temp (°C)
D78/H88	58	D88/H97b	−55
D88/H78	115	D97a/H88	40
D88/H97a	45		

IV. Conclusion

Approximating random poly(ethylene–butene-1) with LCT homopolymers is demonstrated to represent the temperature dependence of χ. Furthermore, the LCT interaction energies derived from SANS χ data are found to predict the UCST transitions. However, much more experimental data, e.g., SANS, properties of mixing *P–V–T*, and phase transitions, are needed to test fully LCT.

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