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Relation of Effective Interaction Parameters for Binary Blends and Diblock Copolymers: Lattice Cluster Theory Predictions and Comparisons with Experiment

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ABSTRACT: The generalized lattice cluster theory of polymers with structured monomers is used to compute and compare the effective interaction parameter χ_{eff} and phase diagrams for diblock copolymer melts and the corresponding binary blends. Predictions are given for general variations of both χ_{eff}'s and phase diagrams with thermodynamic state and molecular weights for PS-*b*-PMMA, PS-*b*-PVME, and PEP-*b*-PEE diblock copolymer melts and the corresponding blends. The three microscopic interaction energies for the PS-*b*-PMMA and PEE-*b*-PEP systems are obtained from fits to small-angle neutron scattering data, while those for PS-*b*-PVME melts are taken from our fits to scattering and excess thermodynamic data for the corresponding PS/PVME blend. The junction point in diblock copolymer chains is found to provide an additional large $1/M$ destabilizing contribution to χ_{eff}. Calculations performed for an incompressible model cannot explain the small-angle neutron scattering data, and the inclusion of "equation of state effects" (or "compressibility") is necessary.

I. Introduction

Block copolymers exhibit a rich array of interesting phenomena, such as microphase separation, stabilization of blends, and micelle formation (in a homopolymer matrix), which are responsible for the existence of significant scientific and technological interest in these systems. Present theories[1,2] of block copolymers are replete with either untested or clearly oversimplifying assumptions. Examples of these include the approximations that the Flory effective parameter χ_{eff} is identical for block copolymers and binary blends and that χ_{eff} is independent of composition, pressure, and molecular weights. A dependence of χ_{eff} on pressure and composition, in addition to the generally assumed dependence on temperature, implies that χ_{eff} is a function of the thermodynamic state of the block copolymer system or, equivalently, the χ_{eff} depends on "compressibility" or "equation of state effects".

The above customary assumptions generally follow from simple application of Flory–Huggins theory[3] and from the identification of χ_{eff} as proportional to a linear combination of the *microscopic* binary interactions ϵ_{AA}, ϵ_{BB}, and ϵ_{AB}. Our recent lattice cluster theory treatments,[4–8] concerning the influence of monomer structure, local correlations, and compressibility on the thermodynamic properties of binary polymer blends, emphasize the fact that χ_{eff} and more generally the three independent quantities χ_{AA}, χ_{BB}, and χ_{AB} for a compressible system are effective *macroscopic* interaction parameters (i.e., thermodynamic properties) and as such are functions of the *microscopic* interaction energies ϵ_{AA}, ϵ_{BB}, and ϵ_{AB}. Thus, the three thermodynamic χ's depend on thermodynamic state (pressure, temperature, and composition) as well as on molecular weights.

By analogy with other thermodynamic properties, the molecular weight dependence of the three macroscopic interaction parameters is anticipated as having the form $\chi = a + b/M$ in the large molecular weight (M) limit, with the correction term b/M being an end effect, partially arising because monomers at the chain ends are different from those internal to the chain. A series of model computations[4–8] and ones for PS/PVME blends[5,7] find b_{eff} for $\chi_{\text{eff}} = \chi_{AA} + \chi_{BB} = 2\chi_{AB}$ to generally be negative, thereby providing a stabilizing influence from the chain ends.

The passage to block copolymers maintains the fact that the three χ's are still thermodynamic properties, which therefore depend on thermodynamic state, local correlations, monomer structure, and molecular weights. The introduction of the junction in a diblock copolymer leads to the expectation that the three χ's vary with molecular weight as $\chi = a + b/M + j/M$, where the additional contribution j arises from $1/M$ corrections associated with the presence of the junction.[9] It would be expected that a_{eff} and b_{eff} in the incompressible limit should become identical to those for a binary blend of the same components. However, allowance for compressibility implies that the three a's and b's depend on thermodynamic state. Consequently, the a's may incur additional $1/M$ dependences through the equation of state. Any $1/M$ dependences to the χ's are especially relevant because experiments on diblock copolymers often use fairly low molecular weights to place the microphase separation temperature within convenient ranges. Thus, it is anticipated that χ should differ between block copolymers and blends.

Computations for a PS-*b*-PMMA melt indicate[9] that the junction contribution far exceeds that from chain ends ($|j| \gg |b|$) and that j is generally positive and therefore destabilizing with respect to microphase separation. A brief analysis of the data of Russell et al.[10] for a PS–PMMA melt shows that an incompressible lattice cluster theory cannot describe their data for χ_{eff} and the small-angle neutron scattering function $S(k)$; the system must be taken as compressible. Furthermore, Tang and Freed[11] demonstrate that allowing χ_{eff} for an incompressible diblock copolymer to have a simple quadratic composition dependence drastically alters the phase diagram for microphase transitions. Thus, it is essential to develop a molecular-based theory for the thermodynamic properties of diblock copolymer melts.

This paper extends the preliminary investigation[9] in paper I on the dependence of χ_{eff} and of the homogeneous → bcc microphase transition temperature T_{ODT} for diblock copolymers on monomer structure, composition, temperature, pressure, and molecular weights. Because both of these properties are determined from the peak in $S(k)$ for $k^* \neq 0$, they are, in fact, not pure thermodynamic quantities and therefore are not presently amenable to

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computation by the lattice cluster theory of polymer systems with structured monomers. However, as noted in paper I without the derivation now provided, the compressible random phase approximation (CRPA)[12] may be combined with the lattice cluster theory to enable calculation of the partial structure factors $S_{\alpha\beta}(k)$ for diblock copolymers and hence the evaluation of χ_{eff} and T_{ODT}. This is possible because the CRPA partial structure factors are functions of the three independent χ_{AA}, χ_{BB}, and χ_{AB} that are evaluated from the lattice cluster theory.

Section II begins by briefly sketching the lattice cluster theory for computation of the thermodynamic properties of diblock copolymers with structured monomers. A generalization is provided of the diblock copolymer CRPA partial structure factors $S_{\alpha\beta}(k)$ to describe components with unequal monomer volumes. These $S_{\alpha\beta}(k)$ are presented as a function of the three $\chi_{\alpha\beta}$. The $k \to 0$ limit $S_{\alpha\beta}(0)$ is used to supply one relation determining the $\chi_{\alpha\beta}$, while two schemes are tried for providing the remaining two relations necessary to enable the three diblock copolymer $\chi_{\alpha\beta}$ to be evaluated from the lattice cluster theory. Section III describes new predictions for a PS-*b*-PMMA system, whereas section IV summarizes the lattice cluster theory predictions for a PS-*b*-PVME melt, a diblock copolymer system which to our knowledge has not yet been made. Our impetus here stems from the fact that we have made extensive comparisons[5,7,8] of the lattice cluster theory predictions with experiments on PS/PVME blends. Therefore, values of the three microscopic interaction energies ϵ_{AA}, ϵ_{BB}, and ϵ_{AB} are available. However, the general positive nature of the junction correction j, noted above, naively leads to the expectation of diminished miscibility of the diblock copolymer melt over that for the blend, and our computations are designated to determine whether these simple expectations are borne out by detailed computations. Section V then analyzes the neutron scattering and rheological measurements of Bates et al.[13] for PEP-*b*-PEE melts to assess the relevance of the $1/M$ contributions to χ_{eff} for this system. Readers more interested in comparison with experiments and predictions may skip to section III.

II. Compressible RPA Theory for Structure Factor in Diblock Copolymer Systems

A. Model of Diblock Copolymer Melts. A single diblock copolymer chain is composed of two covalently bonded homopolymer chains. The standard lattice model of a diblock copolymer melt represents each chain with two sets (blocks) of sequentially bonded monomers lying at the sites of a regular array with N_{l} total lattice sites. Monomers of type α (α = A, B) are joined by $N_\alpha - 1$ flexible backbone bonds, with a single bond providing the junction between two blocks. The melt free volume is modeled by the presence of n_{v} unoccupied sites (called voids) with volume fraction $\phi_{\text{v}} = n_{\text{v}}/N_{\text{l}}$.

A major limitation of the standard lattice model lies in taking monomer and void volume to be equal. This limitation is removed in the generalized lattice model by allowing single monomers of both blocks to have specified molecular structures that cover s_α neighboring lattice sites. The athermal limit diblock copolymer melt is, therefore, characterized by the number of chains n, the monomer structures, and the two site occupancy indices $M_{\text{A}} = N_{\text{A}}s_{\text{A}}$ and $M_{\text{B}} = N_{\text{B}}s_{\text{B}}$ (or equivalently by the ratio $m_{\text{A}} = M_{\text{A}}/M$, where $M = M_{\text{A}} + M_{\text{B}}$), with N_α still designating the degree of polymerization.

Interactions in polymer systems generally involve short-range repulsions and longer range attractions. The former are naturally described by excluded volume constraints which prohibit any two submonomer units to lie at the same lattice site, while the latter are introduced by ascribing the attractive microscopic van der Waals energy $\epsilon_{\alpha\beta}$ to nearest neighbor portions of monomers α and β. Since all portions of a monomer are assumed, for simplicity, to be energetically equivalent, there are only three microscopic attractive energies ϵ_{AA}, ϵ_{BB}, and ϵ_{AB}. In reality, different subgroups in a monomer interact with differing energies. Although the lattice cluster theory may be formulated with group specific interactions, the limitation to three averaged energies is made here for both algebraic and conceptual simplicity.

B. Theory for Partial Structure Factors $S_{\alpha\beta}(k)$. The compressible RPA analysis of Tang and Freed[12] provides scattering functions for the standard model of diblock copolymer melts in which both monomer types and the voids occupy equal volumes. We require the generalization of this CRPA treatment to a diblock copolymer system in which monomers have internal structures and extend over several lattice sites. This extension yields the slightly modified expression

$$S_{\alpha\beta}(k) = \{(-1)^{1-\delta_{\alpha\beta}} J_{\alpha\beta}[G_{\text{AA}}(k)G_{\text{BB}}(k) - G_{\text{AB}}(k)^2] + \phi_{\text{v}}G_{\alpha\beta}(k)\}/\{[-2(\chi_{\text{AA}} + \chi_{\text{BB}} - 2\chi_{\text{AB}}) + 4\phi_{\text{v}}(\chi_{\text{AA}}\chi_{\text{BB}} - \chi_{\text{AB}}^2)][G_{\text{AA}}(k)G_{\text{BB}}(k) - G_{\text{AB}}(k)^2] + J_{\text{AA}}G_{\text{AA}}(k) + J_{\text{BB}}G_{\text{BB}}(k) + 2J_{\text{AB}}G_{\text{AB}}(k) + \phi_{\text{v}}\} \tag{2.1}$$

where the $J_{\alpha\beta}$ are related to the macroscopic interaction parameters $\chi_{\alpha\beta}$ between α–β subunit pairs by

$$J_{\alpha\beta} \equiv 1 - 2\chi_{\alpha\beta}\phi_{\text{v}} \tag{2.2}$$

and where the k-dependent functions $G_{\alpha\beta}(k)$ are defined as

$$G_{\alpha\alpha}(k) = (1 - \phi_{\text{v}})m_\alpha M_\alpha S_{\text{D}}^{(\alpha)}(k), \quad \alpha = \text{A, B} \tag{2.3a}$$

$$G_{\text{AB}}(k) = (1 - \phi_{\text{v}})m_{\text{A}}M_{\text{B}}[1 - {}^1/_2k^2R_{\text{A}}^{\;2}S_{\text{D}}^{(\text{A})}(k)]\,[1 - {}^1/_2k^2R_{\text{B}}^{\;2}S_{\text{D}}^{(\text{B})}(k)] \tag{2.3b}$$

The single-chain structure factor $S_{\text{D}}^{(\alpha)}(k)$ for the α block (α = A, B) is traditionally approximated by the ideal Debye function

$$S_{\text{D}}^{(\alpha)}(k) = D(k^2R_\alpha^{\;2}) = \frac{2}{k^2R_\alpha^{\;2}}\left[1 - \frac{1}{k^2R_\alpha^{\;2}}\{1 - \exp(-k^2R_\alpha^{\;2})\}\right] \tag{2.4}$$

and the radii of gyration R_α in (2.3) and (2.4) are assumed to be ideal, i.e., proportional to the unperturbed Kuhn lengths l_α

$$R_\alpha = ({}^1/_6N_\alpha)^{1/2}l_\alpha \tag{2.5}$$

The quantity $m_\alpha = M_\alpha/(M_{\text{A}} + M_{\text{B}})$ in (2.3) represents the fraction of lattice sites occupied by α monomers in a single diblock copolymer chain and replaces the traditional composition variable $f = N_{\text{A}}/(N_{\text{A}} + N_{\text{B}})$ appearing in RPA formulas for equal monomer volumes.[12] Likewise, the monomer structure dependent site occupancy indices $M_\alpha = N_\alpha s_\alpha$ replace the polymerization indices N_α in (2.3).

Our previous paper[8] introduces a procedure for computing the CRPA partial structure factors $S_{\alpha\beta}(k)$ for homopolymer blends by using the lattice cluster theory. This method considers the $k = 0$ limits of $\{S_{\alpha\text{B}}(k)\}$ and expresses the three unknown macroscopic interaction parameters $\chi_{\alpha\beta}$, appearing also in (2.1), as functions of the three independent binary blend thermodynamic quantities $S_{\alpha\beta}(0)$ that are evaluated from the lattice cluster theory. However, in contrast to binary blends, the $S_{\alpha\beta}(0)$ for diblock copolymer melts become simply proportional to each other and hence are linearly dependent. The $k = 0$

limit implies $[G_{AA}(k)G_{BB}(k) - G_{AB}(k)^2] = 0$ and $S_D{}^{(A)}(k) = S_D{}^{(B)}(k) = 1$. Consequently, the diblock copolymer partial structure factors (2.1) simplify to

$$S_{\alpha\beta}(0) = [\phi_v m_\alpha M_\beta]/[(1 - 2\chi_{AA}\phi_v)m_A M_A + (1 - 2\chi_{BB}\phi_v)m_B M_B + 2(1 - 2\chi_{AB}\phi_v)m_A M_B + \phi_v/(1 - \phi_v)] \tag{2.6}$$

where the only dependence on α and β appears through the trivial numerator factor of $m_\alpha M_\beta$. Equation 2.6 demonstrates that the three $S_{\alpha\beta}(0)$ are not independent in the sense that it is not possible to invert (2.6) and determine the three macroscopic interaction parameters $\chi_{\alpha\beta}$ in terms of the three $S_{\alpha\beta}(0)$ without introducing additional assumptions.

Because the individual $S_{\alpha\beta}(0)$ in a diblock copolymer melt are not linearly independent in the above-described sense, we consider their sum

$$S_{\mathrm{tot}}(0) = S_{AA}(0) + 2S_{AB}(0) + S_{BB}(0) \tag{2.7}$$

which is a thermodynamic quantity. Substituting (2.6) into the right-hand side of (2.7) produces a single relation between the three macroscopic $\chi_{\alpha\beta}$ and the total structure factor $S_{\mathrm{tot}}(0)$

$$S_{\mathrm{tot}}(0)^{-1} = \frac{1}{\phi_v} + \frac{1}{M(1 - \phi_v)} - 2[\chi_{AA}m_A{}^2 + \chi_{BB}m_B{}^2 + 2\chi_{AB}m_A m_B] \tag{2.8}$$

The latter, on the other hand, may be evaluated from the Helmholtz free energy F_c as

$$S_{\mathrm{tot}}(0)^{-1} = \left.\frac{\partial^2[F_c/(N_l k_B T)]}{\partial(1 - \phi_v)^2}\right|_{T,V} \tag{2.9}$$

Introduction of the lattice cluster theory free energy in (2.9) and use of eq 2.8 yield one relation containing the three $\chi_{\alpha\beta}$. This relation is then combined below with lattice cluster theory computations and two additional relations in order to evaluate the $\{\chi_{\alpha\beta}\}$.

Our generalized lattice cluster theory[14] produces the diblock copolymer melt free energy F_c as a polynomial in the polymer volume fraction $\phi = (1 - \phi_v)$

$$\frac{F_c}{N_l k_B T} = \phi_v \ln \phi_v + \frac{1 - \phi_v}{M} \ln \frac{2(1 - \phi_v)}{M} + \frac{M - 1}{M}(1 - \phi_v)[\ln z - 1] + \sum_{i=1} g_c{}^{(i)}(1 - \phi_v)^i \tag{2.10}$$

The coefficients $g_c{}^{(i)}$ depend on monomer molecular structures, molecular weights, and the diblock composition fraction m_α. The coefficients are evaluated as expansions in the inverse lattice coordination number ($1/z$) and in the three microscopic interaction energies $\epsilon_{\alpha\beta}$ in units of k_BT. Our computations retain only linear terms in $\{\epsilon_{\alpha\beta}\}$ and employ a hypercubic lattice with coordination number $z = 6$. The void free volume fraction ϕ_v is determined for a given pressure from the equation of state that follows upon differentiating (2.10). Lengthy technical details of the new lattice cluster diagrams that are required for generating these $\{g_c{}^{(i)}\}$ of diblock copolymers will be presented elsewhere.[14]

Because eqs 2.7 to 2.10 provide only one relation for determining the three $\chi_{\alpha\beta}$, we introduce two different limiting assumptions that permit evaluation of χ_{AA} and χ_{BB} from the lattice cluster theory. The first assumption takes χ_{AA} and χ_{BB} for a diblock copolymer melt to be the same functions of ϕ_v as in pure homopolymer melts

$$\chi_{\alpha\alpha} = \chi^{\circ}_{\alpha\alpha}, \quad \alpha = A, B \tag{2.11}$$

This assumption is, perhaps, most reasonable under situations where the corresponding A–B binary blend is phase separated and there is little "screening" of α–α interactions by β monomers. Substituting the choice (2.11) into eq 2.8 enables the determination of the interaction parameter χ_{AB} as

$$\chi_{AB} = \frac{1}{2m_\alpha m_\beta}\left\{-\frac{1}{2}\left[S_{\mathrm{tot}}(0)^{-1} - \frac{1}{\phi_v} = \frac{1}{M(1 - \phi_v)}\right] - \chi^{0}_{AA}m_A{}^2 - \chi^{0}_{BB}m_B{}^2\right\} \tag{2.12}$$

with the understanding that $S_{\mathrm{tot}}(0)$ is calculated from the lattice cluster theory for the diblock copolymer melt, while the $\{\chi^{\circ}_{\alpha\alpha}\}$ are calculated from the lattice cluster theory for homopolymer melts. The pure homopolymer melt interaction parameters $\chi^{\circ}_{\alpha\alpha}$ simply follow from the LCT Helmholtz free energy $F_0{}^{(\alpha)}$ as polynomials in polymer composition $\phi = (1 - \phi_v)$

$$\chi^{\circ}_{\alpha\alpha} = -\frac{1}{2}\left[\left.\frac{\partial^2[F_o{}^{(\alpha)}/(N_l k_B T)]}{\partial(1 - \phi_v)}\right|_{V,T} - \frac{1}{\phi_v} - \frac{1}{M_\alpha(1 - \phi_v)}\right] = \sum_{i=0} \chi_{\alpha\alpha}{}^{(i)}(1 - \phi_v)^{(i)} \tag{2.13}$$

The pure melt free energy $F_0{}^{(\alpha)}$ is also obtained from the LCT and has an identical general structure to (2.10). Thus, the coefficients $\chi_{\alpha\alpha}{}^{(i)}$ again depend on monomer structure, molecular weight, and dimensionless microscopic interaction energy $\epsilon_{\alpha\alpha}/k_BT$.

The second approximation replaces χ°_{AA} and χ°_{BB} in (2.12) by the χ^{b}_{AA} and χ^{b}_{BB} for a binary blend with the same free volume fraction ϕ_v as in the diblock copolymer melt and with $\phi_A/\phi_B = m_A/m_B$. Such a replacement is mathematically well defined even when the corresponding binary blend is phase separated; however, this second approximation is probably physically more reasonable when the corresponding binary blend has a stable homogenous phase under the same thermodynamic conditions. Section III shows that this second choice leads to strong inconsistencies with experimental data for homogeneous phase diblock copolymers near the microphase separation temperature. Thus, the computations in sections III–V use the first approximation.

In addition to eq 2.8, there exists another independent equation involving the three interaction parameters $\chi_{\alpha\beta}$. This equation relates the internal energy of a diblock copolymer melt to an integral over k of a function containing the structure factor $S(k)$. Since the latter is a complicated function of the $\{\chi_{\alpha\beta}\}$ [see (2.1)], only a numerical solution can eventually be obtained. But even then, it is not possible to determine three independent $\chi_{\alpha\beta}$ because of the lack of a third independent equation. Therefore, the assumption of (2.11) seems to be forced upon us.

If the scattering by monomers of type α occurs with complete contrast (i.e., only one type of monomers scatter), the observed structure factor is

$$S(k) = S_{\alpha\alpha}(k) \tag{2.14}$$

while incomplete contrast leads to the more general formula

$$S(k) = p_A^2 S_{AA}(k) + 2p_A p_B S_{AB}(k) + p_B^2 S_{BB}(k) \qquad (2.15)$$

where the reduced scattering lengths p_A and p_B are normalized such that $p_A - p_B = 1$. Computations are readily performed in both cases.

Small-angle neutron scattering data for diblock copolymer melts are generally analyzed using incompressible RPA scattering functions $S_{\alpha\alpha}^I(k)$. This IRPA analysis is used to extract an effective Flory interaction parameter $\chi_{\rm eff}$ between A and B monomer subunits. The $\chi_{\rm eff}$ is customarily interpreted as a measure of microscopic interactions in the block copolymer system and is subsequently introduced into theories of interfacial properties in microphase-separated block copolymers and in phase-separated binary blends.

Because of the prior focus on $\chi_{\rm eff}$, we apply the traditional IRPA analysis[1] to our lattice cluster theory computations in order to determine how monomer molecular structure and compressibility affect $\chi_{\rm eff}$. The effective Flory interaction parameter $\chi_{\rm eff}$ is traditionally defined for diblock copolymer melts by

$$\chi_{\rm eff} = -\frac{1}{2}[S(k^*) - F_M^I(k^*)] \qquad (2.16)$$

where $S(k)$ is the experimental scattering function, k^* corresponds to the wavevector for which this $S(k)$ has a maximum

$$\left.\frac{\partial S(k)}{\partial k}\right|_{k=k^*} = 0 \qquad (2.17)$$

and $F_M^I(k)$ is determined from the incompressible RPA theory in terms of the incompressible limit $\{G_{\alpha\beta}^I(k)\}$ of the $G_{\alpha\beta}(k)$ functions (see eqs 2.3) as

$$F_M^I(k) = \frac{G_{AA}^I(k) + G_{BB}^I(k) + 2G_{AB}^I(k)}{G_{AA}^I(k)G_{BB}^I(k) - G_{AB}^I(k)^2} \qquad (2.18)$$

Our compressible diblock melt LCT computations of $S(k)$ are substituted in (2.16) to give $\chi_{\rm eff}$. These calculations require specification of N_A and N_B, monomer structures, Kuhn lengths, temperature, and pressure. The LCT predictions are compared in the following sections with experiments and contrasted with assumptions inherent in the incompressible RPA analysis, where $\chi_{\rm eff}$ is often assumed to be a single composition, etc., independent constant that varies inversely with absolute temperature.

III. Comparison with Experiments and Predictions for PS-*b*-PMMA Melts

Our previous short communication[9] (paper I) compares lattice cluster theory computations with experimental data of Russell et al. for small-angle neutron scattering from PS-*b*-PMMA melts. Several additional features of this comparison and some new predictions are provided here. Figure 1 displays the monomer structures for styrene and methyl methacrylate that are used in our computations which are based upon a simple cubic lattice with $z = 6$.

The lattice cluster theory free energy and CRPA scattering functions depend on the three microscopic site–site (see Figure 1) interaction energies $\epsilon_{\rm S\text{-}S}$, $\epsilon_{\rm S\text{-}MMA}$, and $\epsilon_{\rm MMA\text{-}MMA}$, which are treated as the only adjustable parameters. However, our analysis[5] of neutron scattering and excess thermodynamic properties for PS/PVME blends has already determined $\epsilon_{\rm S\text{-}S}$, so this parameter is fixed at its value from ref 5. The remaining two interaction energies are the only adjustable parameters and are obtained by fitting the data for $\chi_{\rm eff}$ as a function of temperature for one PS-*b*-PMMA sample with $f = N_{\rm PS}/(N_{\rm PS} + N_{\rm PMMA}) = 0.44$ and $N = N_{\rm PS} + N_{\rm PMMA} = 262$. (The small polydispersity is neglected.)

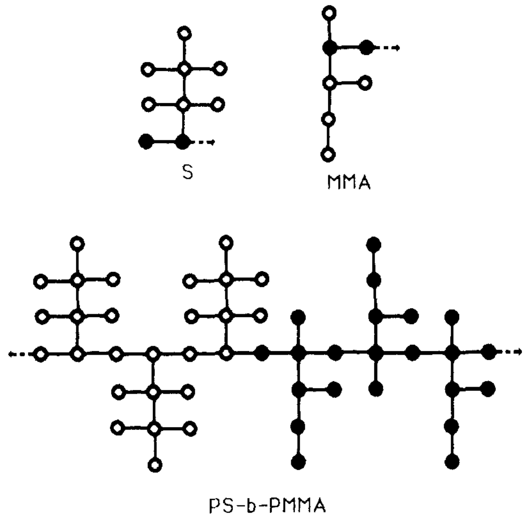

Figure 1. Models of the monomer structures for styrene (S) and methyl methacrylate (MMA) as well as of the junction structure in a PS-*b*-PMMA diblock copolymer chain. Circles depict portions of monomers on single lattice sites, and lines depict flexible bonds. Solid circles in monomer structures designate monomer fragments lying on the backbone chain, and arrows indicate the directions of linkages between monomers on continuation of the blocks.

An alternative procedure for determining $\epsilon_{\rm MMA\text{-}MMA}$ (and also $\epsilon_{\rm S\text{-}S}$) is to use equation of state (*PVT*) data for the homopolymer melts, but the lowest pressure, for which complete and accurate enough data exist, appears to be about 100 atm. More limited PS data of Quach and Simha[15] at 1 atm yield $\epsilon_{\rm S\text{-}S}$ in the range of 0.45 k_BT_0 to 0.5 k_BT_0 with $T_0 = 415.15$ K. The former is consistent with the value $\epsilon_{\rm S\text{-}S} = 0.5\,k_BT_0$ obtained by us in ref 5. However, empirical values of ϵ_{ii} must depend on pressure because an increase in pressure leads to more repulsive average interactions. Thus, it is rather dangerous to extrapolate a fitted ϵ_{ii} from more extensive *PVT* data at 100 atm to a pressure of 1 atm where the neutron scattering experiments of Russell et al.[10] are performed. In addition, the calculated small-angle neutron scattering intensities at 1 atm seem to be more sensitive to the ϵ_{ii} but less sensitive to the cell volume than are calculated *PVT* melt properties. Therefore, the two unknown microscopic interaction energies $\epsilon_{\rm S\text{-}MMA}$ and $\epsilon_{\rm MMA\text{-}MMA}$ are chosen to reproduce the experimental data of Russell et al.[10]

Because the $k \rightarrow 0$ limit of the CRPA for diblock copolymer melts provides only one relation defining the three macroscopic $\chi_{\alpha\beta}$, two alternatives are described in section II for chosing the $\chi_{\alpha\alpha}$. Reference 9 displays the excellent fit to the experimental data that is obtained when the $\chi_{\alpha\alpha}$ are set equal to pure melt $\chi_{\alpha\alpha}^{\circ}$. (No fit is found when using an incompressibility assumption.) The fit in ref 9 yields $\epsilon_{\rm S\text{-}MMA} = 0.486445\,k_BT_0$ and $\epsilon_{\rm MMA\text{-}MMA} = 0.4753\,k_BT_0$. The large number of significant figures presented for $\epsilon_{\rm S\text{-}MMA}$ arises from our attempt to exactly reproduce the experimental data for $S(k)$. The above fit assumes complete contrast in the scattering, but computations with incomplete contrast produce almost identical results. In addition, the computed transition temperature for microphase separation (estimated from the temperature at which $S(k^*)$ diverges) is in good agreement with observations.

Our earlier paper[9] presents CRPA–lattice cluster computations of the scattering intensity $S(k)$ assuming complete contrast in the scattering and determining $l_1 = l_2 = l_{\rm eff}$ from the location of the experimental k^*. The choice of a common $l_{\rm eff}$ follows the assumption of Russell et al. and is partly motivated by experimental uncertainty in $l_{\rm PMMA}$. The theory allows the use of different l_α or of altered

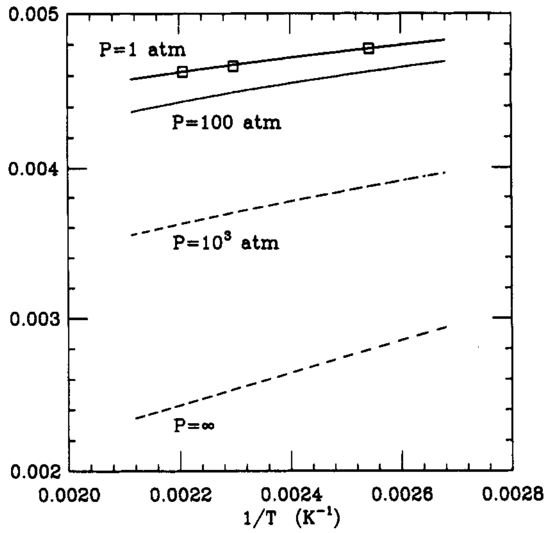

Figure 2. Lattice cluster theory predictions of the pressure and temperature dependence for $\chi_{\rm eff}$ of a PS-*b*-PMMA melt for f = 0.44, N = 262, and interaction parameters as in the text. Squares designate the experimental points, and the curve provides our computations.

chain dimensions in the block copolymer system.[9] Figure 3 in paper I demonstrates that the CRPA reasonably well reproduces the experimental data for $S(k)$.

If the $\chi_{\alpha\alpha}$ are instead chosen as lattice cluster theory interaction parameters $\chi_{\alpha\alpha}{}^{b}$ for a blend with the same molecular weights as in the diblock copolymer, it is not possible to reproduce the $1/T$ behavior of $\chi_{\rm eff}$ that is observed by Russell et al.[10] The choice of $\chi_{\alpha\alpha}{}^{b}$ leads to a computed $\chi_{\rm eff}$ that is a parabolic function of $1/T$, rather than the observed linear dependence. Furthermore, the computed transition to a bcc ordered phase then becomes qualitatively unreasonable as it displays jump discontinuities. These findings are not unexpected because under the experimental conditions we predict the homogeneous blend phase to be unstable. In addition, Monte Carlo simulations by Fried and Binder[16] and a scaling analysis by Tang and Freed[17] indicate that the two blocks become locally segregated for temperatures near the microphase separation temperature. Thus, the pure melt $\chi_{\alpha\alpha}$ are more likely to describe the proper physical situation corresponding to the experimental conditions, so all subsequent computations employ the pure melt $\chi^{0}_{\alpha\alpha}$.

Given the fit of $\epsilon_{\rm S\text{-}MMA}$ and $\epsilon_{\rm MMA\text{-}MMA}$ to the data of Russell et al., it is interesting to predict the expected behavior of $\chi_{\rm eff}$ [defined by (2.16)] as a function of pressure, temperature, molecular weights, etc. Figure 2 presents lattice cluster theory computations of $\chi_{\rm eff}$ as a function of T^{-1} for a range of pressures between 1 atm and the incompressible limit $P = \infty$. As discussed above, the $\{\epsilon_{\alpha\beta}\}$ are expected to vary with pressure, so Figure 2 is understood to provide a guide to general trends. A striking feature of Figure 2 is the large difference, mostly of entropic origin, between $\chi_{\rm eff}$ for P = 1 atm and $P = \infty$. Other computations[9] for low molecular weight diblock copolymers exhibit $\chi_{\rm eff}$ as having a similar large entropic contribution that is greatly diminished upon passage to the incompressible limit. Thus, the blocks are more incompatible than would be predicted by using blend data for $\chi_{\rm eff}$. Moreover, the entropic component of $\chi_{\rm eff}$ for low molecular weight block copolymers is considerably larger than that for the corresponding binary blend. This arises because $\chi_{\rm eff}$ for blocks contains large coefficients of $1/N$ corrections that emerge from correlations associated with the the junction region. An additional large entropic contribution arises from the distribution of free volume in the diblock copolymer melt (equation of state effects). Computations for blends show that $\chi_{\rm eff}$ may either increase or decrease with increasing pressure, but our computations for diblocks have so far only found a decrease.

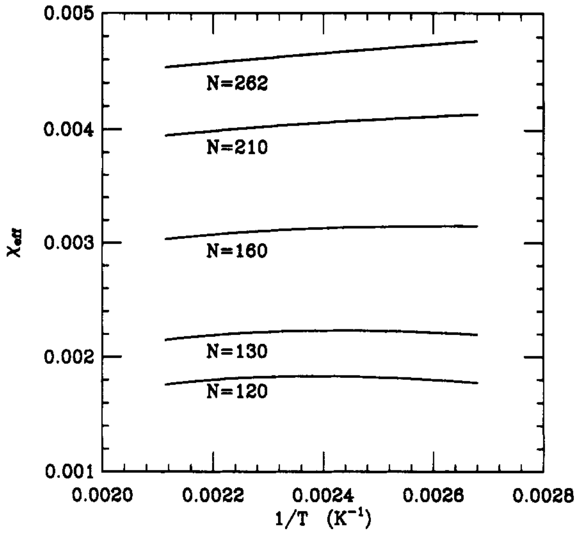

Figure 3. Lattice cluster theory predictions of the temperature and polymerization index (N) dependence for $\chi_{\rm eff}$ of a symmetric PS-*b*-PMMA melt (f = 0.5) at P = 1 atm for interaction parameters given in the text.

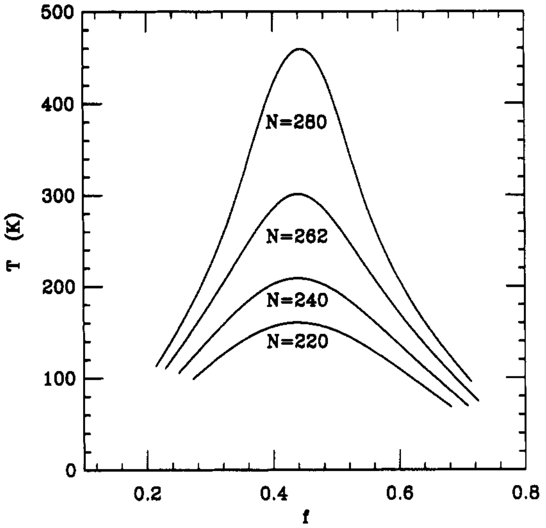

Figure 4. Lattice cluster theory predictions of the polymerization index (N) dependence of the order–disorder transition temperature for PS-*b*-PMMA at P =1 atm.

Figure 2 displays the variation of the computed $\chi_{\rm eff}$ vs T^{-1} as a function of pressure, partially reflecting the variation in effective contact probabilities as free volume is squeezed out of the system. The strong molecular weight dependence of $\chi_{\rm eff}$ is further illustrated in Figure 3. A similar molecular weight dependence persists in the incompressible (high pressure) limit, but the entropic part of $\chi_{\rm eff}$ is greatly reduced. While the curves for higher N in Figure 3 are fairly linear, they become slightly parabolic at lower N. This curvature does not appear in calculations for the incompressible limit.

The temperature at which $S(k^*)$ diverges provides an approximation to the location of the homogeneous → microphase transition temperature, which in the Leibler theory[1] corresponds to a transition to a bcc phase. Our previous paper[9] predicts the pressure dependence for PS-*b*-PMMA (note the caveat above), and Figure 4 extends the predictions to the polymerization index dependence. The variation of the critical temperature T_c with N in Figure 4 is stronger than would be expected from the Leibler theory,[1] which assumes an N-independent $\chi_{\rm eff}$ and obtains $\chi_c N = 10.5$ (symmetric case) as determining T_c for

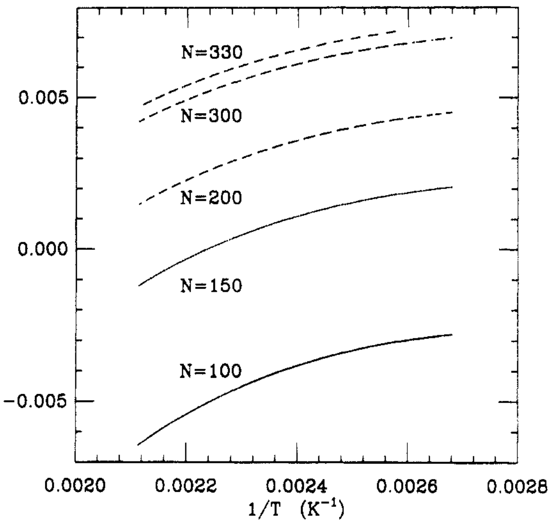

Figure 5. Lattice cluster theory predictions of the temperature and polymerization index dependence of χ_{eff} for a symmetric PS-*b*-PVME ($f = {}^1/_2$) melt at $P = 1$ atm using parameters from ref 5.

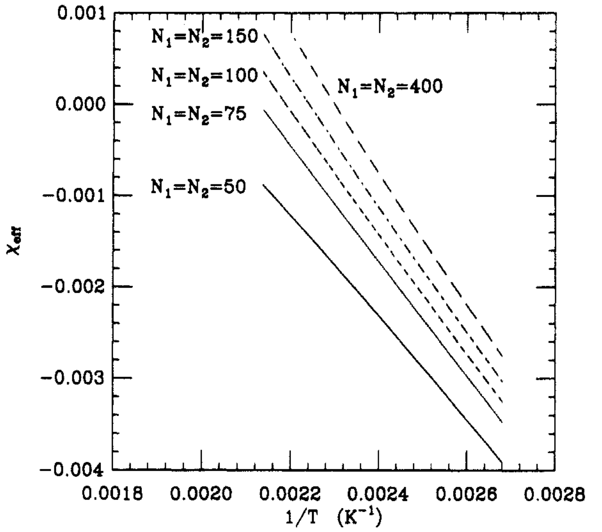

Figure 6. Same as Figure 5 for a PS/PVME blend with $\Phi_1 = \phi_1/(1 - \phi_v) = {}^1/_2$.

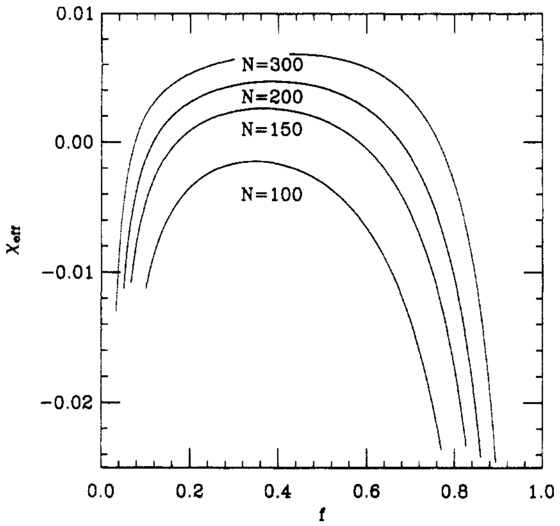

Figure 7. Lattice cluster theory predictions of the composition and polymerization index dependence of χ_{eff} for a symmetric PS-*b*-PVME melt ($f = {}^1/_2$) at $P = 1$ atm and $T = 393.15$ K using interaction energy parameters from ref 5.

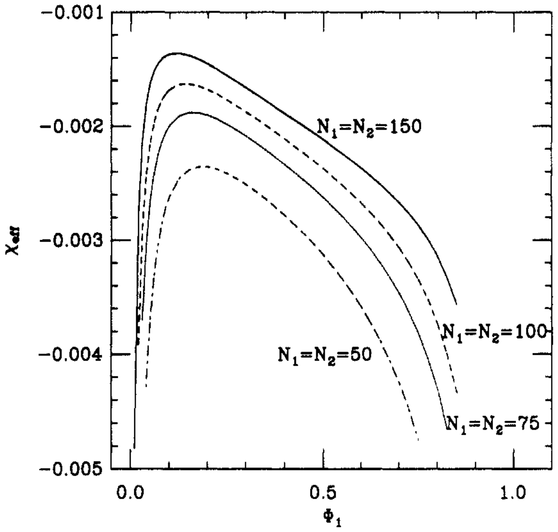

Figure 8. Same as Figure 7 but for a PS/PVME blend.

$N \rightarrow \infty$. The large variation in Figure 4 emerges because of the significant N-dependent entropic component to χ_{eff}. Nevertheless, for a given composition f, the transition temperature still satisfies the relation $\chi_c(N)N = C(f)$, where $C(f)$ is a constant.

IV. Predictions for the PS-*b*-PVME System

The large entropic contribution to χ_{eff} of low molecular weight diblock copolymers suggests that it might be interesting to study diblocks formed from highly compatible homopolymers. Such systems may even undergo microphase separation because of the additional unfavorable entropic part of χ_{eff} that is imparted by the junction between the blocks. Thus, lattice cluster combinations are provided in Figures 5, 7, 9, and 11 for a PS-*b*-PVME melt to contrast the corresponding behavior of compatible PS/PVME blends in Figures 6, 8, 10, and 12. All interaction parameters are taken from our previous fits[5] of lattice cluster theory computations to experimental data for PS/PVME blends, so there are are no new adjustable parameters. The styrene monomer structure is the same as that in Figure 1, while that for vinyl methyl ether is the obvious united-atom chemical structure with two backbone and two side group units (see ref 5). Figure 5 presents the computed polymerization index and temperature dependence of χ_{eff} for symmetric PS-*b*-PVME ($f = 0.5$) homogeneous-phase diblock copolymer melts. Notice again the strong N dependence and the large entropic contribution. Despite this entropic $1/N$ contribution to χ_{eff}, the computed density variation is roughly 0.2% over the range of N in Figure 5. The behavior in Figure 5 contrasts sharply with that calculated for corresponding symmetric blends in Figure 6, where the variation of χ_{eff} with inverse temperature is linear and opposite. The slope in Figure 6 is negative and indicative of a system with attractive net exchange interactions, while the temperature-dependent slope in Figure 5 is positive and hence displays the typical behavior of systems with net repulsive exchange interactions. The slope in Figure 6 becomes more negative for increasing N, indicating a positive enthalpic $1/N$ contribution, while the $1/N$ entropic contribution is negative as found in extensive model computations for binary blends.[4,6]

Figures 7 and 8 for diblocks and blends, respectively, exhibit somewhat similar composition and polymerization index variations of the corresponding χ_{eff}. However, note the generally large diblock values, which arise from the presence of the junction. Because PS and PVME are quite miscible (exhibiting a LCST), the addition of a junction to form PS-*b*-PVME and the concomitant unfavorable junction entropy might be expected to produce a LCST type phase diagram for the order–disorder transition. However, the situation is quite different as displayed in Figure 9, where the order–disorder transition is predicted

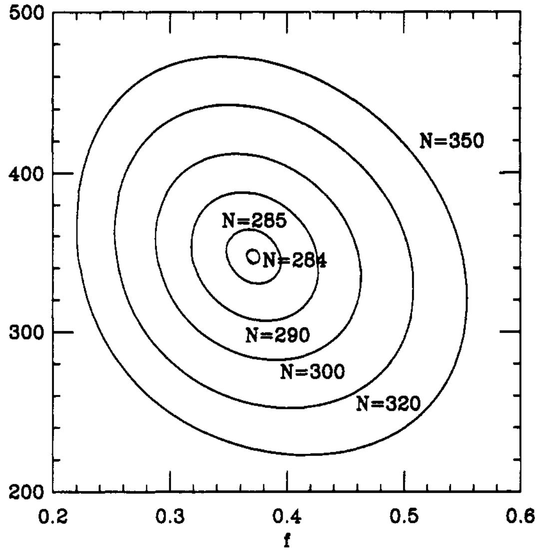

Figure 9. Lattice cluster theory predictions of the composition (f) and polymerization index (N) dependence of the order–disorder transition temperature for a PS-*b*-PVME melt at P = 1 atm using interaction energy parameters from ref 5.

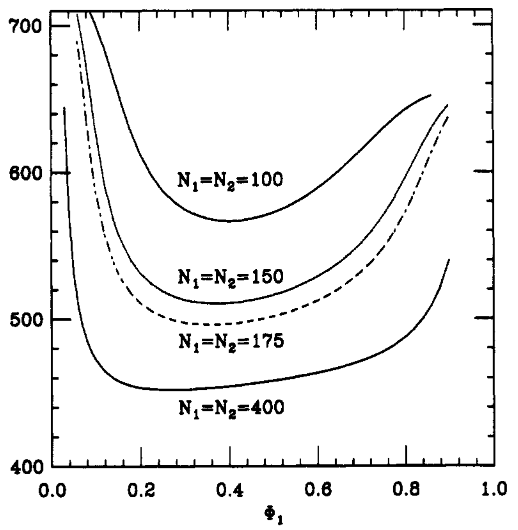

Figure 10. Lattice cluster theory predictions of the phase diagram for PS/PVME blends at P = 1 atm.

to be re-entrant and strongly molecular weight dependent. The LCST composition in Figure 9 increases with N, while the UCST composition decreases with N. No microphase separation is predicted for sufficiently small N. To our knowledge, no experiments have yet been made for PS-*b*-PVME systems. The known LCST behavior of PS/PVME blends[18] is displayed in Figure 10, which presents the spinodal for different polymerization indices N. The critical composition contains more PVME as N increases, and this is consistent with $\epsilon_{\rm VME\text{-}VME}$ being the most attractive of the three microscopic interaction energies.[8] The predicted pressure dependences of the order–disorder and spinodal transitions are given in Figures 11 and 12, respectively. These figures can only provide qualitative illustration because the ϵ_{ij} are taken as pressure independent, whereas the van der Waals interactions must become less attractive at higher pressures.

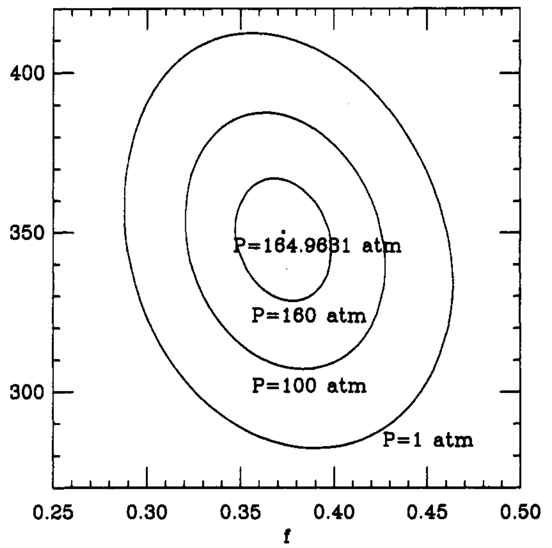

Figure 11. Same as Figure 9 but showing the pressure dependence for the polymerization index N = 300.

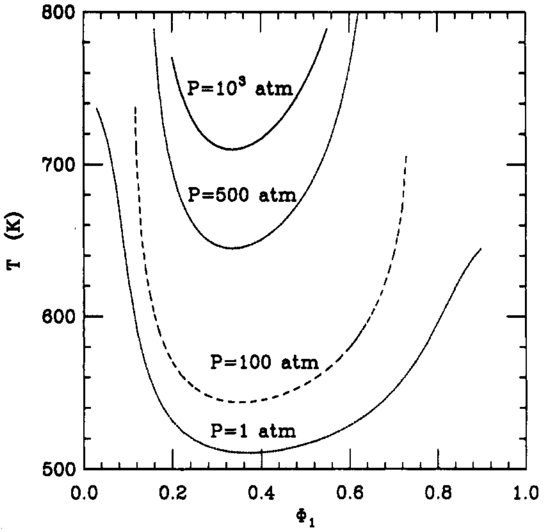

Figure 12. Same as Figure 10 but showing the pressure dependence for the polymerization indices $N_1 = N_2 = 150$.

V. Comparison with Experiments and Predictions for the PEP-*b*-PEE Melt

Another interesting set of experimental data for diblock copolymer melts is provided by Bates et al.[13] and concerns the scattering intensities of one PEP-*b*-PEE sample (f = 0.55) at three temperatures and rheological determinations of the order–disorder transition temperature $T_{\rm ODT}$ for three PEE-*b*-PEP samples with different molecular weights. Fits to experimental rheology data by Bates et al.[13] assume that the effective interaction parameter $\chi_{\rm eff}$ has the conventional form

$$\chi_{\rm eff} = A + B/T \tag{5.1}$$

where both constants $A = 4.4 \times 10^{-4}$ and B = 4.9 K are assumed to be N independent. On the other hand, our lattice cluster theory computations suggest that $\chi_{\rm eff}$ from neutron scattering experiments should contain $1/N$ contributions for the N = 1026 PEP-*b*-PEE sample studied by Bates et al. Our fits to the scattering data of Bates et al.[13] yield A and B that depart from values reproducing the $T_{\rm ODT}$ rheology data. Thus, by permitting both A and B to linearly depend on $1/N$, we are able to make $\chi_{\rm eff}$ fit both sets of the Bates et al. data simultaneously with

$$\chi_{\rm eff} = (-0.002913 + 7.04885/N) + \frac{3.8647 - 1322.8/N}{T} \tag{5.2}$$

The entropic portion of $\chi_{\rm eff}$ in (5.2) is almost entirely dominated by the $1/N$ contribution, whereas the enthalpic part is mainly N independent, but with nonnegligible $1/N$ corrections. The dominant $1/N$ entropic term in (5.2) and the primarily N-independent enthalpic portion of $\chi_{\rm eff}$ are quite consistent with a wide range of lattice cluster theory computations, some of which are described in the two previous sections.

While the above phenomenological analysis[9] from paper I stresses the importance of $1/N$ contributions, it is useful to apply the lattice cluster theory directly to the scattering data of Bates et al.[13] The monomer structures for PEP and PEE blocks are the obvious united-atom chemical structures with $s_{\rm PEP} = 5$ and $s_{\rm PEE} = 4$, respectively. We find that the observed scattering intensities $S(k)$ at three temperatures are insufficient for uniquely specifying the three (adjustable) microscopic interaction energy parameters $\epsilon_{\alpha\beta}$ in a compressible theory (an incompressible theory is again inadequate). Many fits are possible, and additional experimental data are required for a unique fit. A typical fit, which exactly reproduces the scattering data but which provides a slightly low order–disorder transition temperature, is obtained for $\epsilon_{11} = 0.45863\ k_{\rm B}T_0$, $\epsilon_{22} = 0.44799\ k_{\rm B}T_0$, and $\epsilon_{12} = 0.44444799\ k_{\rm B}T_0$ with $T_0 = 415.15$ K. The effective interaction parameters $\chi_{\rm eff}$ [expressed on a per lattice site basis and computed using (2.16) and lattice cluster theory calculations of $S(k)$] are $\chi_{\rm eff}(T = 399.15{\rm K}) = 0.0024090$, $\chi_{\rm eff}(T = 424.15{\rm K}) = 0.0023756$, and $\chi_{\rm eff}(T = 454.75{\rm K}) = 0.0023059$. The above choice of the $\{\epsilon_{\alpha\beta}\}$ leads to the calculated $T_{\rm ODT} = 384.9$ K (determined from the divergence of $S(k^*)$) which is by about 11 K lower than our estimate of the transition temperature from the $S(k^*)$ data of Bates et al.[13] Since our calculations do not account for fluctuations, the calculated transition temperature should be higher than the observed $T_{\rm ODT} = 396$ K. By adjusting the $\{\epsilon_{\alpha\beta}\}$, it is presumably also possible to reproduce the $T_{\rm ODT}$, which are, however, very sensitive in the theory to the magnitude of the microscopic exchange energy $\epsilon \equiv \epsilon_{11} + \epsilon_{22} - 2\epsilon_{12}$ and also to experimental errors in determining $S(k^*)$ that affect the accuracy of our fits. Paper I, for example, shows[9] how allowance for experimental errors in $S(k^*)$ for a PS-*b*-PMMA melt may produce a difference in computed critical temperatures of about 30 K. Calculations in ref 9 indicate that polydispersity should influence $T_{\rm ODT}$, but here we focus on the general trends. The main point of the analysis in this section is to emphasize again that both entropic and enthalpic portions of $\chi_{\rm eff}$ for diblock copolymer melts must be N dependent. The customary neglect of a molecular weight dependence to the effective interaction parameters for these systems leads to inconsistent fits for different types of measurements.

VI. Discussion

By analogy with a compressible binary polymer blend,[8] there are three macroscopic interaction parameters $\chi_{\alpha\beta}$ for a compressible diblock copolymer melt. Each interaction parameter $\chi_{\alpha\beta}$ is a function of all three microscopic interaction energies $\epsilon_{\alpha\beta}$ in the simplest model that assumes all subunits of a given monomer are energetically equivalent. However, the diblock copolymer macroscopic interaction parameter $\chi_{\rm eff}$ is defined [see (2.16)] by the maximum in $S(k)$ and is thus not a thermodynamic quantity. This difficulty is overcome by introducing the assumption that $\chi_{\rm AA}$ and $\chi_{\rm BB}$ are the same as in the pure homopolymer melts. An alternative limiting choice involves taking the $\chi_{\alpha\alpha}$ to be the self-interaction parameters in the corresponding binary blends, but this choice is strongly inconsistent with experimental small-angle neutron scattering data. Therefore, our lattice cluster theory–compressible random phase approximation computations employ the first approximation. It is rather nontrivial to derive another two independent equations which would enable the unique determination of the three $\chi_{\alpha\beta}$ without resorting to any additional assumption.

Our lattice cluster theory computations of the effective parameter $\chi_{\rm eff}$ for various diblock copolymer systems exhibit a strong molecular weight dependence of $\chi_{\rm eff}$. Since the formation of a diblock copolymer homogeneous phase requires that chains not be too long (otherwise microphase separation occurs), the $1/N$ corrections to the Flory–Huggins mean field approximation become especially relevant. The dominant $1/N$ contributions are those associated with the junction region, and they are mainly responsible for different effective interaction parameters $\chi_{\rm eff}$ for diblock copolymer melts and the corresponding binary blends. Ignoring the molecular weight dependence of $\chi_{\rm eff}$ leads to discrepancies in the $\chi_{\rm eff}$ calculated from two different types of experimental data (rheological and neutron scattering measurement) for PEP-*b*-PEE.[13]

It is particularly difficult to test experimentally the common belief that $\chi_{\rm eff}$ for blocks and corresponding blends are identical. This is partially because the stability regions for both of these systems generally do not overlap. While, for example, a symmetrical PS-*b*-PMMA diblock copolymer chain with polymerization index $N = 262$ has a stable (or metastable) homogeneous phase slightly above 300 K, the corresponding binary blend is calculated[9] to be stable only above 700 K, but even then the computed homogeneous phase is unphysically dilute. In order to make a direct comparison between blend and block $\chi_{\rm eff}$'s, we have performed lattice cluster theory computations for a PS-*b*-PVME melt and for a PS/PVME blend using microscopic interaction energies found from our previous fits[5] to data for neutron scattering[18] and excess thermodynamic properties[19] of PS/PVME blends at $P = 1$ atm. Figures 5 and 6 clearly contrast the differences in $\chi_{\rm eff}$'s between the blend and diblock, and this difference is emphasized by the two $\chi_{\rm eff}$'s displaying opposite temperature dependences. The phase diagrams are also extremely different: we compute a closed loop order–disorder transition phase diagram versus the observed[18] (and computed[8]) blend spinodal curve with a lower critical solution temperature. Because the three average microscopic interaction energies $\epsilon_{\alpha\beta}$ are taken as pressure independent, the predicted general pressure variations of $\chi_{\rm eff}$ (see Figure 2) and of phase diagrams in Figures 11 and 12 must be taken as only qualitative guides.

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