

Molecular modeling of polymer blends: Stabilization of blends by block copolymers

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Abstract: The lattice cluster theory provides systematic corrections to Flory-Huggins theory from the presence of local correlations in a polymer system. The theory employs a generalized lattice model which describes structured monomers as extending over several lattice sites. The theory also includes the influence of "equation of state effects" into the statistical thermodynamics of multicomponent polymer blends. We describe applications of the lattice cluster theory to explain the properties of polymer blends and diblock copolymers and to provide new predictions for the stabilization of blends by block copolymers.

INTRODUCTION

Flory-Huggins (FH) theory¹ is widely used to describe the thermodynamic properties for a rich variety of polymer systems. The theory represents the thermodynamic properties in terms of a phenomenological interaction parameter χ whose properties are deduced by fitting theory to experimental data. While this venerable theory exhibits several notable successes, it is well known that many of its predictions are in conflict with observations and that many practical questions cannot be explained within the framework of FH theory and its variants. We illustrate some of these points by specific reference to binary polymer blends and their mixtures with diblock copolymers, systems for which the lattice cluster theory^{2,3,4,5,6,7} has been developed to alleviate some of the most serious deficiencies of FH theory.

Although FH theory itself may be derived without recourse to a lattice model, we employ the original lattice model formulation because the simplifications posed by a lattice model make such formulations the most tractable mathematically. When applied to polymer blends, FH theory produces the well-known free energy of mixing ΔF^{mix} as

$$\frac{\Delta F^{\text{mix}}}{N_1 kT} = \frac{\phi_1}{M_1} \ln \phi_1 + \frac{\phi_2}{M_2} \ln \phi_2 + \chi \phi_1 \phi_2, \quad (1)$$

where ϕ_i is the volume fraction of species i , M_i is the number of lattice sites occupied by a chain of species i , N_1 is the total number of lattice sites, kT is the thermal energy, and χ is the famous Flory interaction parameter which *emerges from FH theory* in the form,

$$\chi = z(\epsilon_{11} + \epsilon_{22} - 2\epsilon_{12})/2kT, \quad (2)$$

where z is the lattice coordination number (the number of nearest neighbor lattice sites) and ϵ_{ij} are the attractive nearest neighbor van der Waals interaction energies. The FH theory of (2) *predicts* that χ is inversely proportional to T and is independent of composition, molecular weights, pressure, etc. Unfortunately, however, the empirical χ , *defined by (1)*, often displays a substantial, temperature independent portion (called the entropic χ) and a rich composition dependence, both of which are unexplained by FH theory. The ultimate goal of statistical mechanical theories for polymer fluids lies in providing a molecular based understanding of the origins^{4,6,7,8} for the entropic χ and for the composition and other dependences of both the entropic and enthalpic χ . The composition dependences of the entropic and enthalpic χ are, perhaps, the most crucial quantities for explaining the phase behavior of polymer systems. Thus, a molecular theory of these composition dependences is central to understanding the thermodynamics of polymer systems. Before describing such a theory, we note that the distinction between miscible and immiscible polymer blends may involve differences in the exchange energy $\epsilon = \epsilon_{11} + \epsilon_{22} - 2\epsilon_{12}$ by as little as tens of calories per mole of repeat units, energy differences that are much too small to be computed by currently available or foreseeable quantum mechanical or molecular mechanics

methods. Thus, the desired molecular theory must describe general trends and employ empirical information to fix values for $\epsilon_{\alpha\beta}$.

THEORY SECTION

The deficiencies of Flory-Huggins theory may arise because the lattice model over simplifies reality, because the elementary approximations of Flory are inadequate, or both. The lattice cluster theory²⁻⁷ (LCT) demonstrates that both features are insufficient and contribute to the inadequacies of FH theory. The LCT improves the latter by including contributions from local correlations and the former by specifying structures for individual monomers. Hence, the monomers in the generalized lattice model are permitted to occupy several lattice sites according to molecular size and shape.

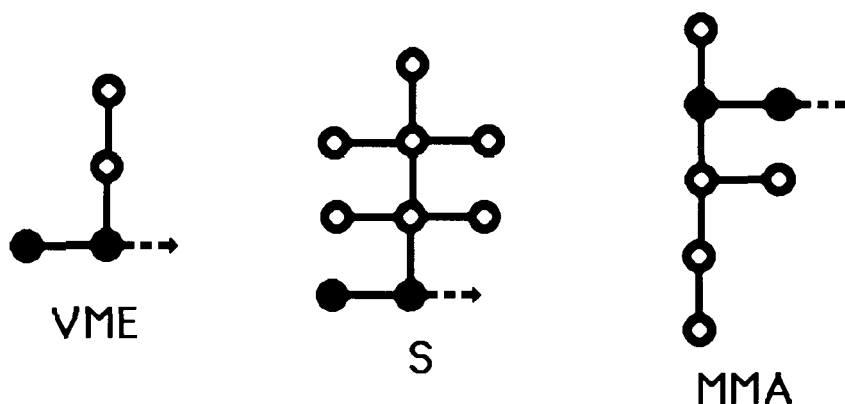


Fig. 1. Monomer structure models for vinylmethylether (VME), styrene (S), and methylmetacrylate (MMA).

Figure 1 exhibits three examples of vinyl monomer structures used in the LCT computations described below. Filled circles designate submonomer units lying on the chain backbone, while the open circles are units in the side groups. Lines designate bonds that are completely flexible in three dimensions. (Figure 1 represents monomer structures in two-dimensions only for the sake of presentation.) The generalized lattice model of polymer systems is solved using cluster expansion methods⁵⁻⁷ which describe the influence on thermodynamic properties of short range packing and interaction induced correlations. Classic FH theory emerges as the zeroth order approximation in which all correlations are neglected. Vacant sites are permitted in order to model the excess free volume that is necessary for defining the pressure and for deriving the equation of state. The units of free volume are, therefore, smaller than monomer sizes, a feature more realistic than provided by a simple extension of Flory-Huggins theory to compressible systems in which voids have the same size as monomers (or as the Kuhn effective segments).

The LCT provides the free energy of mixing for a multicomponent system (with or without solvent) in the general form⁶

$$\frac{\Delta F_{\text{mix}}}{N_i kT} = \sum_i \frac{\phi_i}{M_i} \ln \phi_i + \phi_v \ln \phi_v + \sum_i g_i(\phi_i) \phi_i \phi_v + \sum_{i \neq j} g_{ij}(\{\phi_k\}) \phi_i \phi_j, \quad (3)$$

where ϕ_v is the void volume fraction that is determined as a function of pressure, temperature, composition, and molecular weights from the equation of state, $g_i(\phi_i)$ is the non-combinatorial free energy for a pure melt of species i at volume fraction ϕ_i , and $g_{ij}(\{\phi_k\})$ is the contribution from pairs of species. The LCT explicitly demonstrates that $g_{ij}(\{\phi_k\})$ is *not pairwise additive* as is customarily assumed in many phenomenological thermodynamic models. The LCT obtains^{6,8,9} the $g_i(\phi_i)$ and $g_{ij}(\{\phi_k\})$ as polynomials in volume fractions, with coefficients computed as double expansions in $1/z$ and in $\epsilon_{\alpha\beta}/kT$. Coefficients in the expansion are dependent on monomer structures, molecular weights, and chain architectures (linear, branched or networks). The greater mathematical simplicity of lattice models enables us to derive the *single* analytic expression (3) which is valid for all compositions, molecular weights, interaction energies $\epsilon_{\alpha\beta}$, monomer structures, and temperatures (provided the $\epsilon_{\alpha\beta}/kT$ are small). While the full expressions for $g_i(\phi_i)$ and $g_{ij}(\{\phi_k\})$ are somewhat lengthy, these algebraic formulas are easily processed numerically.

The LCT with its extended lattice model immediately explains the origins of the entropic FH χ as arising from the local packing constraints and correlations when the system contains polymer chains with different monomer sizes and shapes. The high pressure, high molecular weight limit of the entropic χ is represented in terms of simple geometrical characteristics of the monomer molecular structures, but interesting corrections appear at finite pressures and molecular weights. Likewise, the lattice cluster theory exhibits χ as having a molecular weight dependence and a rich variation with composition^{9,10}, both in accord with experimental observations. The correlation corrections to the FH χ of (2) stress the fact that χ is a general thermodynamic quantity which must therefore be a function of thermodynamic state, i.e., temperature, composition, molecular weights, etc. Thus, the limiting high molecular weight χ must develop some $1/M$ corrections at lower molecular weights due to the inequivalence of end monomers and those interior to the chain.

Lattice cluster theory predictions have been tested by parameter free direct comparison with Monte Carlo simulations¹¹ of the identical lattice model for a polymer-solvent system. Simulations indicate that the LCT is very accurate at higher temperatures, but small errors of roughly 5-10% in the internal energies of mixing become noticeable at lower temperatures of $kT/\epsilon = 3$. The comparison with recent simulations¹² further demonstrate that the influence of monomer structure is likewise adequately described at higher temperatures. Additional tests for polymer blends would be desirable as these systems possess much less size asymmetry than does the polymer-solvent system. Given the available tests demonstrating that the LCT provides an accurate representation of the exact solution to the extended lattice model, we have considered several comparisons with experiment to extract a deeper molecular understanding of factors governing blend properties.

The LCT computations^{9,13,14,15} exhibit a strong sensitivity of the composition dependence of χ to monomer structures and local correlations, an important feature in explaining a wealth of experimental data concerning small angle neutron scattering¹⁶ (SANS) data, excess thermodynamic data,¹⁷ and even local structural properties¹⁶ of blends. Other LCT computations^{18,19} for diblock copolymers predict a large $1/M$ junction contribution to χ and a novel re-entrant type of phase diagram for microphase separation. A more recent application¹⁰ of the LCT theory focuses on the subtle properties of isotopic blends. Our computations for PSD/PSH blends indicate²⁰ that the observed composition dependence of the SANS χ arises primarily from equation of state effects and that simple models based on differences between the polarizabilities of the isotopomers are inadequate for explaining the influence of H/D isotope effects on the PSD/PSH blend χ . The LCT provides simultaneous fits to the SANS data²¹ as well as to both the coexistence curve²² and the interfacial profile²² in the phase separated PSD/PSH blend. The following discussion illustrates some of these LCT computations, including a treatment in progress for blend stabilization by diblock copolymers²³.

COMPARISONS WITH EXPERIMENT AND NOVEL PREDICTIONS

Because polystyrene (PS) and poly(vinyl methyl ether) (PVME) are quite miscible, their blends are widely studied experimentally, thereby providing tests of available theories for polymer blends. Han *et al.*¹⁶ present extensive SANS data for the effective interaction parameter χ^{eff} . The extrapolated zero angle neutron scattering intensity $S(0)$ is used to define χ^{eff} by

$$1/S(0) = 1/(M_1\phi_1) + 1/(M_2\phi_2) - 2\chi^{\text{eff}}. \quad (4)$$

(FH theory yields $\chi^{\text{eff}} = \chi^{\text{FH}}$.) The Han *et al.* data¹⁶ are unique in covering a broad range of both compositions and temperatures, and they are available for three samples with rather different molecular weights M_1 and M_2 . Most importantly, the data display χ^{eff} as having a rich composition dependence and a significant entropic component. In addition, there are data on the spinodal curves and on the small angle scattering $S(k)$ (for nonzero k) which probes structure and correlations in the blends.

It is common in treating small angle neutron scattering data to assume blend incompressibility, whereupon the only free parameter in the LCT computations is the exchange energy ϵ , and this is chosen simply to reproduce a single data point¹⁶ for χ^{eff} (at $T = 142\text{C}$ and $\phi_1 = \phi_{\text{PSD}} = 0.1$). To make matters more interesting, the parameter-free LCT computations of χ^{eff} are performed¹³ for 66 model binary blends, constructed from polymers having twelve different monomer structures of the types represented in Fig. 1. The degree to which several of these models can reproduce the experimental data provides some measure of the importance of monomer molecular structure in determining blend properties. Four of these

different models are found to reproduce the substantial composition dependence of χ^{eff} over the full temperature and molecular weight range, but these cases fail to explain the magnitude of the heat of mixing ΔH^{mix} data of Shiomi *et al.*¹⁷ The best of these models produces ΔH^{mix} that differs from experiment by roughly a factor of 5. Moreover, Shiomi *et al.*¹⁷ also find that the volume change on mixing ΔV^{mix} is as large as 0.3%, indicating, as is well known, that the PS/PVME blend is not an incompressible system. The compressibility of PS/PVME blends is also intimately related to the existence of a lower critical solution temperature phase diagram for this system.

The compressible version of the LCT employs three adjustable parameters ϵ_{11} , ϵ_{22} , and ϵ_{12} , which appear nonlinearly in the LCT formulas^{6,9} for the blend thermodynamic properties. The extensive neutron scattering data for χ^{eff} alone are insufficient to determine these three parameters. A good fit to the scattering data may be obtained¹³ using rather unphysical models for the blend in which the vinyl methyl ether (VME) monomer is taken to be large and bulky, while the styrene (S) monomer is chosen as very small and compact. However, when the compressible LCT is required simultaneously to fit all the data for χ^{eff} , ΔH^{mix} , and ΔV^{mix} , only one of the 66 model blends is successful in reproducing the data. The VME and S monomers in this model blend are represented by structures given in Fig. 1. The VME structure is identical to the correct united atom structure, while the S monomer in Fig. 1 is the closest approximation to the size and shape of styrene among the 12 possibilities considered. Figure 2 exhibits the fit of the compressible LCT to a selected portion of the SANS data¹⁶ for the H sample, while fits to the

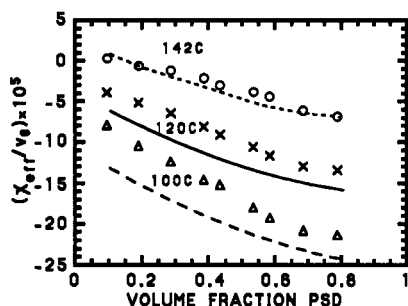


Fig. 2. Comparison of LCT computations with SANS data of Han *et al.*¹⁶ for PS/PVME blends.

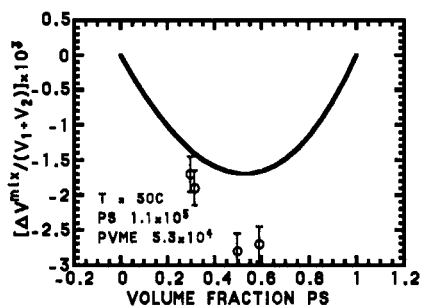


Fig. 3. Comparison of LCT computations with data for ΔV^{mix} from Shiomi *et al.*¹⁷ for PS/PVME blends.

ΔV^{mix} data are given in Fig. 3. The LCT computations contain only three adjustable parameters, the microscopic interaction energies $\epsilon_{S,S}$, $\epsilon_{S,VME}$, and $\epsilon_{VME,VME}$. Nevertheless, the theory reasonably reproduces^{8,13} the temperature, composition, and molecular weight dependence of the SANS χ . (The temperature of 100C is close to the PSD glass transition temperature, and generally the theoretical curves better represent the experimental data at higher temperatures.) More, importantly Fig. 3 shows that the theory with the same parameters also describes the volume change on mixing ΔV^{mix} . Not shown are fits to χ at other temperatures and for other molecular weight samples as well as fits^{13,14,15} to the heat of mixing ΔH^{mix} , the spinodal curve, the correlation length, and the apparent radius of gyration. Fits to ΔH^{mix} data are found in Ref. 13, where the theory computations are in error by a factor of roughly 2. It is possible to improve the agreement of the LCT with experiment by recognizing that, for instance, the O atom in the VME monomer has different interaction energies than do the CH and CH₂ groups of this monomer. Including these group-specific interactions into the LCT would certainly lead to improved fits of the experimental data but at the expense of greatly increasing the number of adjustable parameters. Most important, however, is the fact that the simplest model with three averaged microscopic energies $\epsilon_{\alpha\beta}$ demonstrates the strong sensitivity of blend properties to monomer structures, local correlations, and "equation of state effects." (All compressible LCT computations are performed for a pressure of 1atm.)

Even the fit of the incompressible version of the LCT to the neutron scattering data is significant in the sense that the theory *with just a single adjustable parameter* is capable of describing the rich composition, temperature, and molecular weight dependence of the experimental χ^{eff} . This situation stands in marked contrast to predictions of simple one parameter FH theory with its composition and molecular weight

independent χ parameter. This success of even the incompressible LCT stresses the importance of including into the theory the influence of monomer structures and local correlations. However, it is often illusory to base tests of a theory for such complicated materials as polymer blends on data obtained only from one type of measurement. The requirement of also reproducing data for ΔH^{mix} and ΔV^{mix} indicates the necessity for extending the theory to describe the system as compressible. Moreover, several benefits accrue from this extension despite its requirement for having three adjustable parameters. Ref. 15 presents the spinodal curve as calculated from the compressible LCT without recourse to additional adjustable parameters. The agreement with the Han *et al.* data¹⁶ is again very good. Moreover, the power of the LCT is further demonstrated by comparing its predictions^{14,15} with the $k \neq 0$ structural information obtained from the small angle neutron scattering $S(k)$. The LCT computations yield $\epsilon_{S,S}$ as less attractive than $\epsilon_{S,VME}$. Naturally this implies that PVME is a good solvent for PS, a prediction consistent with the observation of expanded PS chains for low concentrations of PS in PVME. Likewise, LCT computations find $\epsilon_{VME,VME}$ as more attractive than $\epsilon_{VME,S}$, and this is consistent with PVME being contracted when present as a dilute component in the blend. Furthermore, $\epsilon_{VME,VME}$ is more attractive than $\epsilon_{S,S}$, and this is consistent with the fact that the critical composition is rich in PVME, the component with the stronger self-attraction. This interesting analysis indicates¹⁴ a strong inter-relation between LCT descriptions of thermodynamic and structural properties, an important component of a full statistical mechanical theory. Thus, the (admittedly highly averaged) LCT interaction energies $\epsilon_{\alpha\beta}$ may have some real microscopic physical meaning, unlike the plethora of FH χ parameters in the literature.

Additional interesting insights emerge from application of the LCT in conjunction with the compressible random phase approximation²⁴ to block copolymer systems. Neutron scattering data are more limited for the disordered phase of these systems, but the availability of $\epsilon_{S,S}$ from the analysis of PS/PVME blends has enabled a LCT treatment of PS-*b*-PMMA diblock copolymers with just $\epsilon_{S,MMA}$ and $\epsilon_{MMA,MMA}$ as the only two adjustable parameters of the theory. (The data are insufficient to consider using perturbed statistical segment lengths.) Our theory predicts a rather strong dependence of χ^{eff} for diblock copolymers on polymerization index N for the following rather clear physical reasons: As noted above, the physical difference between end segments and the internal monomer segments implies the existence of $1/N$ contributions to the χ^{eff} of binary blends and diblock copolymer melts. [These contributions are generally computed as small and negative when using the definition in Eq. (4).] Similarly, the junction in diblock copolymers introduces an additional $1/N$ contribution to χ^{eff} which is customarily defined in terms of the maximum in $S(k)$. The LCT junction contribution to χ^{eff} is generally positive and rather large, especially in view of the fact that experiments on microphase separation in block copolymer systems are often performed for samples with small N . The LCT computations^{18,19} indicate the possibility of incurring significant errors in simply assuming the equivalence of χ parameters for binary blends and the corresponding diblock copolymers.

Given the available LCT $\epsilon_{\alpha\beta}$ for PS, PVME, and PMMA, it is possible to predict^{18,19} the microphase separation transition temperatures T_s for diblock copolymers formed therefrom, as well as the pressure dependence of T_s , which to our knowledge have not yet been determined experimentally. An interesting prediction¹⁹ emerges for the PS-*b*-PVME system where LCT calculations indicate a re-entrant microphase separation with an ordered phase existing at intermediate temperatures and compositions (for a range of N) and a disordered phase at higher and lower temperatures. (The latter, however, lies below a glass transition temperature.) A related phase diagram has been observed by Russell *et al.*²⁵ for PS-*b*-PBMA where the ordered phase occurs at high and low temperatures, while the disordered phase enters at intermediate temperatures. Such a phase diagram is but the photographic negative of that predicted for PS-*b*-PVME and provides general confirmation of the prior predictions as the description of both an upper temperature ordered phase and a re-entrant phase diagram require the inclusion of compressibility in the theory and the treatment of the molecular origins for the composition dependence of χ . Thus, a rich range of physical behaviors is predicted by using the more molecularly based LCT theory.

STABILIZATION OF BLENDS BY BLOCK COPOLYMERS

An important application of block copolymers lies in their ability to stabilize blends. The idea behind this phenomenon is rather simple. Different polymers generally tend to be immiscible, but tying them together in block copolymers forces them to mix (provided the mutual repulsions are not too large). Thus, an A-*b*-B diblock copolymer can stabilize the A/B blend by the presence of favorable A-A and B-B interactions between the homopolymers and the diblock copolymer. Experiments on blend stabilization generally use symmetric diblock copolymers, but the analytical simplicity of the lattice cluster theory enables us to study blend stabilization by highly asymmetric diblocks and also to investigate the influence of diblock

copolymers on miscibility to determine whether the addition of diblocks further enhances the blend's stability. All computations²³ illustrated below are performed for ternary blends at a pressure of 1 atm, and we compute the limit of stability (the spinodal) of a uniform homogeneous phase for fixed diblock volume fraction ϕ_B , but as a function of the composition of the homopolymers.

Figure 4 displays calculated spinodals for a PS/PMMA/PS-*b*-PMMA "symmetric" ternary system characterized by polymerization indices of $N_{PS} = N_{PMMA} = 50$ for the homopolymers and the diblock composition $f = N_{PS}/(N_{PS} + N_{PMMA}) = 1/2$ (with both blocks also having $N = 50$). The interaction energies $\epsilon_{\alpha\beta}$ are taken from previous fits^{18,19} to experimental SANS data²⁶ for PS-*b*-PMMA diblock copolymers and are, of course, not symmetric. The computations summarized in Fig. 4 exhibit the usual blend stabilization expected upon addition of 10-20% of diblock copolymer. The situation in Fig. 5 is, however, quite different. Figure 5 again considers a symmetric blend with $N_{PS} = N_{PMMA} = 50$, but the diblock copolymers are asymmetric with compositions f indicated on the figure. The total diblock polymerization index is still 100 as in Fig. 4, and the diblock volume fraction is fixed at $\phi_B = 0.05$. The symmetric diblock with $f=1/2$ leads to blend stabilization, but the asymmetric diblocks with $f = 0.1, 0.7,$ and 0.9 lead to *destabilization of the blend*. Thus, the use of unsymmetric diblocks provides the possibility for exerting substantial control on the phase diagram and further motivates the consideration of ternary mixtures of block copolymers with miscible blends.

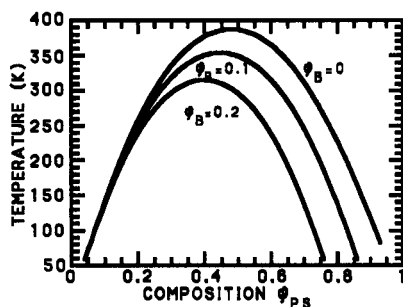


Figure 4. Predicted spinodals for PS/PMMA blend with symmetric PS-*b*-PMMA diblock copolymer and indicated concentrations ϕ_B .

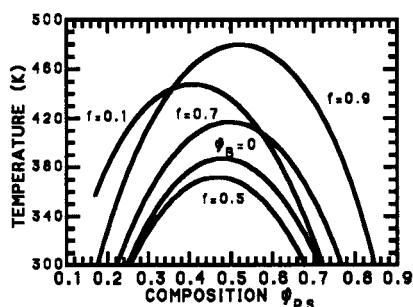


Figure 5. Predicted spinodals for PS/PMMA blend with unsymmetric PS-*b*-PMMA diblock copolymer and indicated compositions f .

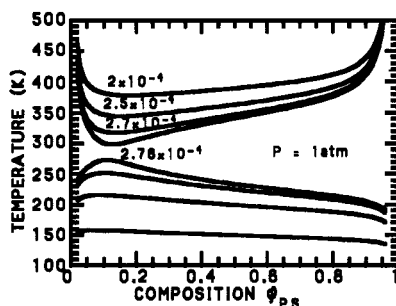


Fig. 6. Predicted spinodals for PS/PVME symmetric blend with symmetric PS-*b*-PVME diblock copolymer and the indicated diblock volume fraction ϕ_B .

The LCT computations for the miscible PS/PVME blend with $N_{PS} = N_{PVME} = 1,000$ and $f = 1/2$ are even more remarkable. Quite minuscule amounts (volume fractions of 10^{-4}) of diblock copolymer produce substantial shifts in the spinodal. The pure blend ($\phi_B = 0$) spinodal is not shown but lies above the top-most curve in Fig. 6. The pure blend has only a lower critical solution temperature, but the ternary systems in Fig. 6 all exhibit both lower and upper critical solution temperatures, with the top-most and

bottom-most curves corresponding to the same ϕ_B . The behavior in Fig. 6 probably arises because the phase separation in PS/PVME blends is strongly influenced by entropic contributions, and consequently the addition of small quantities of diblock copolymers represents a significant perturbation to this entropy.

DISCUSSION

The lattice cluster theory (LCT) provides a significant improvement over Flory-Huggins (FH) theory and other phenomenological theories for the statistical thermodynamics of polymer systems. First of all, the LCT employs an extended lattice model in which monomers are given specific molecular structures by allowing them to extend over several lattice sites. This feature combines with the inclusion of local correlation corrections to simple FH theory to provide predictions of the composition, temperature, molecular weight, etc., dependences of the effective Flory interaction parameter χ whose relation to molecular structure and interactions has heretofore been inaccessible to theory. The LCT predicts the composition dependence of both the entropic and enthalpic contributions to the χ parameter which is probably the most important quantity in determining the phase behavior of multicomponent polymer systems.

The compressibility of polymer melts, blends, and solutions has long been understood to affect thermodynamic properties of these systems. However, in many instances it has been fashionable to ignore the resultant "equation of state effects" in order to formulate the simplest possible zeroth order theory. The LCT computations demonstrate that compressibility also influences the description of small angle neutron scattering data but that additional experimental information may be required to determine the three interaction energies $\epsilon_{\alpha\beta}$ for the simplest model of a binary system. The limited number of applications of the LCT to date currently makes it unclear as to the minimum information required for determining the $\epsilon_{\alpha\beta}$ from experiment, and more applications of the theory should help to resolve this question.

The use of a lattice model has the strong advantages of permitting computations to be performed and of generating from the theory simple, albeit lengthy, analytic formulas for the free energy of multicomponent, compressible polymer systems. The analytic nature of the theory enables a whole host of properties to be computed easily. The latter has enabled us to predict novel phenomena, such as a re-entrant phase diagram for microphase separation of diblock copolymers and the possibility of destabilizing blends by the addition of unsymmetrical diblock copolymers. Computations of this nature are only rendered possible by using the more realistic generalized lattice model, the inclusion of contributions from local correlations, and the relative analytical simplicity of the LCT expressions for the free energy of multicomponent polymer systems. However, it must be emphasized that the lattice model represents an over simplification of reality, and complete quantitative agreement with experiment should never be expected. There are several inadequacies of the current LCT which may be alleviated, and these possible improvements include introducing specific (but not too strong) interactions, the treatment of semiflexibility, and the allowance for the presence of rigid monomers or portions thereof. Some of these extensions are currently being developed.

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