Self-Contacts, Self-Concentration, and the Composition Dependence of the Glass Transition Temperature in Polymer Mixtures

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ABSTRACT: Self-concentration, a consequence of chain connectivity, is an important factor in determining the properties of polymer mixtures. It is proposed that self-concentration has two components. First, there is a “covalent connectivity effect”, which manifests itself in the probability that a site adjacent to a chosen segment on a chain is occupied by a like or unlike segment; second, there is a “conformational connectivity effect” that is a consequence of a chain bending back on itself through both local and long-range factors that depend on the flexibility of the chain. This latter component is modeled using a contact point approach developed in previous work. If the covalent connectivity effect is treated using a lattice model, there is a cancelation of terms and noncovalent contacts do not contribute to self-concentration in calculating the average properties of polymer blends. Nevertheless, when covalent contacts are included together with conformational self-contacts in order to calculate the composition dependence of the glass transition temperature, an equation corresponding to the self-consistent form of the Lodge−McLeish model derived by Lipson and Milner is recovered. In the systems studied so far, this approach leads to consistent results, with values of self-concentration terms that correspond to what would be expected in terms of connectivity and self-contact parameters determined in previous work. This parameter appears to be a transferable constant that depends on the microstructure, conformation and to some degree the molecular weight of the polymer.

Introduction

It has been recognized for quite some time that because of connectivity segments of a polymer chain “see” or interact with more segments of that chain than segments of other chains. This is essentially a consequence of the correlation hole effect described by de Gennes,[1] but such intramolecular contacts were also explicitly accounted for in Huggins original treatment of polymer solutions.[2] In more recent work, considerable interest and much research[3−9] has been inspired by or used the work of Lodge and co-workers,[10−13] who showed how self-concentration effects account for the observation of more than one T_g in miscible systems. This treatment defines an average local composition for each component of the blend. Chain connectivity also leads to local composition fluctuations around a chosen polymer segment or solvent molecule, which would be expected to broaden the observed T_g or T_gs, as described in lattice models by Colby and Lipson[8] and Lipson and Milner.[9]

The Lodge−McLeish model[10] defines an effective local concentration, ϕ_{eff}, as follows:

$$\varphi_{eff} = \varphi_{self} + (1 - \varphi_{self})\langle\varphi\rangle \tag{1}$$

Here $\langle\phi\rangle$ is the total concentration of the component under consideration, and ϕ_{self} is the self-concentration. A self-concentration term, ϕ_{self}, is usually defined for each component of a blend and was originally assumed to be related to the fraction of volume occupied by a Kuhn segment’s length worth of monomers. However, values of ϕ_{self} for a given polymer appear to vary from system to system.[3,4,13] In addition, two distinct T_gs have been observed in certain polymer/diluent systems,[11,14] with a composition dependence that appears very much like those observed in blends, even though the solvent does not have the chain connectivity that leads to a local self-enrichment of its own composition.

In much of the work reported so far, self-concentration appears to have been associated with chain connectivity in a particular way, through the local effect of the covalent connection of a chosen segment to two neighbors (in linear polymers). It has been noted that this approach goes back to the work of Guggenheim,[15] who used a lattice model to derive expressions for the occupancy of pairs of sites by polymer segments and solvent molecules. An equivalent accounting for the occupation of sites was used in recent lattice models describing concentration fluctuations.[8,9] However, as we will argue below, this approach cannot account for noncovalent contacts, because of a cancelation of terms. This approach also suggests that ϕ_{self} will be essentially the same for most polymers, which appears not to be so.

There is another consequence of chain connectivity involving conformations. In work reported more than ten years ago, we developed a model that describes self-contacts in polymer blends and solutions in order to explain systematic differences in fraction of hydrogen-bonded groups observed in homopolymer blends, random copolymers of the same monomers, and mixtures of monomer analogues.[16−19] In addition to the effect of covalent connectivity that can be modeled using Guggenheim statistics, we determined that there is a conformational effect associated with a chain bending back on itself through both local and long-range factors, thus adding a second component to a self-concentration term. This latter effect is in keeping with the ideas of the original Lodge−McLeish model, in that the ability of a chain to fold back on itself, its conformational flexibility, is related to the Kuhn segment length.[10] We will explore this effect in this paper. In addition, this approach leads to some interesting predictions in terms of the dependence of self-concentration on molecular weight, conformation and chain architecture that can be tested in future work. We will start by reviewing our approach to self-contacts, establish a relationship to ϕ_{self} and then show how this accounts for various experimental observations.

Connectivity and Self-Concentration in Polymer Blends and Solutions

In this section, we will consider the extent to which connectivity, in the sense of a chain segment being covalently

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bonded to two of its neighbors, affects self-concentration solely as a result of the probabilities associated with the occupation of pairs of sites. We ask the reader to bear with us here and in the following section, because various notations have been used over the years and although self-contacts and self-concentration are related, they are not identical and need to be defined in terms of different parameters. In what follows, we will follow the conventions adopted in our previous papers,[16,17] where we used the definitions of Guggenheim[15] and Flory[20] to describe surface site fractions and the probabilities of contacts and a notation adopted by Koningsveld and Kleintjens[21] to simplify some of the expressions in the resulting equations. We will then show how this earlier notation relates to definitions of self-concentration.

Guggenheim[15] defined a quantity zq_i, the number of sites neighboring a chain of type i (i.e., those excluding covalently linked neighbors):

$$zq_i = m_i(z-2)+2 \tag{2}$$

where z is the lattice coordination number and m_i is the degree of polymerization of the polymer chain. This equation can be rearranged to give the following form

$$\frac{q_i}{m_i} = 1 - \frac{2}{z}\left(1 - \frac{q_i}{m_i}\right) = 1 - \gamma_l^i \tag{3}$$

where, as in our previous work,[16,17] we defined γ_l^i as follows.

$$\gamma_l^i = \frac{2}{z}\left(1 - \frac{1}{m_i}\right) \tag{4}$$

In this simplification, we utilized the symbol γ following earlier work by Koningsveld and Kleintjens[21] and added the subscript l to distinguish it from a second parameter (γ_s) that we will introduce later to account for a further consequence of connectivity. Neglecting this latter effect for now, we first consider the probability of finding a noncovalently bonded polymer segment adjacent to a chosen segment in a polymer solution which, using Flory's nomenclature,[20] we label θ_i. If we now designate the polymer using the subscript A and the solvent using the subscript B, we have the following equation:

$$\theta_A = \frac{N_A q_A}{N_B + N_A q_A} = \frac{(1-\gamma_l^i)\phi_A}{(1-\gamma_l^i\phi_A)} \tag{5}$$

N_A and N_B are the numbers of molecules of A and B, respectively. This is the same as the probability used by Lipson and Milner[9] in their paper describing local composition effects in polymer−solvent mixtures (their eq 13, with $p(\phi) = \theta_A$ and the assumption that m is large).

To reiterate, this expression describes the probability of finding an A segment adjacent to a chosen A segment to which it is *not* covalently bonded. This is the type of expression that is needed to describe interactions in polymer solutions, but when dealing with the composition dependence of the T_g, it is not only intermolecular vibrations that contribute to the specific heat, C_p, but also skeletal or intrachain lattice modes. In other words, it is necessary to consider neighbors that are also covalently bonded when calculating self-concentration, ϕ_{self}, and local composition, ϕ_{eff}.

The fraction of neighboring sites that are covalently bonded to a chosen segment is $2/z \approx \gamma_l^A$. The probability that a polymer segment occupies one of the remaining $1 - \gamma_l^A$ neighboring sites is given by eq 5, so that the local concentration of A segments is then:

$$\theta_{eff}^A = \gamma_l^A + \frac{(1-\lambda_l^i)^2\phi_A}{(1-\lambda_l^i\phi_A)} \tag{6}$$

This is equivalent to the self-consistent form of the Lodge−McLeish equation for polymer solutions described by Lipson and Milner,[9] with $\gamma_l^A = \phi_{self}^A$, which for high molecular weight polymers is determined by z, the lattice coordination number. (We will consider the self-consistent form of the Lodge−McLeish model in more detail below.)

There are three important consequences of this definition of ϕ_{self}. First, Bernal[22] determined an average coordination number of 9 for the random close packing of spheres. More recent work has shown that spheres appear to be a special case and ellipsoidal objects pack far more efficiently, with a coordination number of about 10.[23,24] This indicates that ϕ_{self}^A should be of the order of 0.20 − 0.22. However, for many polymer/solvent systems and blends values of ϕ_{self} are apparently larger than this. We will return to this point later. Second, in branched systems, particularly those involving hyperbranched polymers and dendrimers, ϕ_{self} and the probability of noncovalent contacts based on eqs 4 and 5 remains the same as in a linear polymer. This is because for every branch point there is an additional chain end, so the value of zq_i in eq 2, hence γ_l^A, is unaltered. Intuitively, one would expect ϕ_{self} to be larger in such systems and infrared measurements on hydrogen-bonded systems indicate that this is indeed so.[25,26] Finally, when describing the average properties of polymer blends (as opposed to concentration fluctuations), the effect of chain connectivity on noncovalent contacts essentially cancels out. For two polymers A and B, the fraction of A segments that are adjacent to a chosen A segment that is not covalently bonded to the first is given by

$$\theta_A = \frac{N_A q_A}{N_A q_A + N_B q_B} = \frac{\phi_A(1-\gamma_l)}{\phi_A(1-\gamma_l) + \phi_B(1-\gamma_l)} = \phi_A \tag{7}$$

Similar arguments apply to the probability that an A segment is next to a B, and so on. We have assumed that packing factors are such that the number of neighbors to A and B can be described by the same coordination number, so that $\gamma_l^A = \gamma_l^B = \gamma_l$, but deviations from this assumption should be small in most systems.

A significant self-concentration effect has been observed in a number of polymer blends and polymer-diluent mixtures and values of ϕ_{self} far greater than ∼0.2 have been required to fit some of this data, implying unreasonably small values of z. In other systems, however, very small values of ϕ_{self} have been determined. According to eq 6 one would expect $\phi_{self} \sim 0.2$ to be a minimum value. We suggest that these discrepancies can be resolved using the Lipson−Milner self-consistent form of the Lodge−McLeish equation and by including a second contribution to self-concentration that has its origin in conformational effects.

Conformational Contributions to Self-Concentration

In order to account for spectroscopic observations, we previously proposed that a chain bends back on itself, both locally and through long-range effects, so that there are an appreciable number of intrachain contacts.[16,17] This is illustrated schematically in Figure 1. We let the fraction of noncovalently bonded same-chain contacts be γ_s^A and γ_s^B, respectively, for the A and B components of a mixture. (We originally called this a "screening" effect, hence the subscript s.) These quantities will depend on chain conformation and architecture in a presumably complex manner, but for blends[16] or polymers in theta solvents[17] we assumed that γ_s^A and γ_s^B have values that are averaged over the distribution of conformations characteristic of the unperturbed Gaussian state and are constants characteristic of a given chain. (In good solvents or dilute solutions γ_s^A and γ_s^B will have smaller values, because of chain expansion.) The probability that a chosen A segment is adjacent to any other A segment, apart from the neighbors to which it is covalently bonded, p_{AA}, is then given by:

$$p_{\mathrm{AA}} = \gamma_s^{\mathrm{A}} + (1-\gamma_s^{\mathrm{A}})\theta_{\mathrm{A}}' \tag{8}$$

It is necessary to introduce additional nomenclature (θ_A') here, because the probabilities or fractions of noncovalent contacts are now given by more complex expressions than those in the preceding section, but as we will show below reduce to the same form when the γ parameters are combined. Essentially, eq 8 states that the fraction of like noncovalent contacts is equal to the fraction of same chain contacts due to conformational effects, γ_s^{A}, plus the fraction of *remaining contacts* multiplied by the fraction of *available interchain contacts of the same type*. This quantity, θ_A', is related to *both* surface site fractions and the fraction of same chain contacts:

$$\theta_{\mathrm{A}}' = \frac{(1-\gamma_s^{\mathrm{A}})\theta_{\mathrm{A}}}{(1-\gamma_s^{\mathrm{A}})\theta_{\mathrm{A}} + (1-\gamma_s^{\mathrm{B}})\theta_{\mathrm{B}}} \tag{9}$$

We therefore have

$$p_{\mathrm{AA}} = \gamma_s^{\mathrm{A}} + \frac{(1-\gamma_s^{\mathrm{A}})^2\theta_{\mathrm{A}}}{(1-\gamma_s^{\mathrm{A}})\theta_{\mathrm{A}} + (1-\gamma_s^{\mathrm{B}})\theta_{\mathrm{B}}} \tag{10}$$

and for the probability of a B next to a chosen A, p_{BA}:

$$p_{\mathrm{BA}} = \frac{(1-\gamma_s^{\mathrm{A}})(1-\gamma_s^{\mathrm{B}})\theta_{\mathrm{B}}}{(1-\gamma_s^{\mathrm{A}})\theta_{\mathrm{A}} + (1-\gamma_s^{\mathrm{B}})\theta_{\mathrm{B}}} \tag{11}$$

Equivalent expressions can be written for the noncovalent contacts of the B chains. These probabilities depend on connectivity in two ways, which for want of better terms we will call covalent connectivity effects, accounted for by the factor γ_l, as described in the preceding section, and conformational connectivity effects, accounted for by the quantity γ_s. However, as noted above (eq 7), for two high polymers we have $\theta_{\mathrm{A}} \approx \phi_{\mathrm{A}}$ and $\theta_{\mathrm{B}} \approx \phi_{\mathrm{B}}$ and the equations are simplified in the sense that there is no dependence on covalent connectivity and z, the lattice coordination number.

$$p_{\mathrm{AA}} = \gamma_s^{\mathrm{A}} + \frac{(1-\gamma_s^{\mathrm{A}})^2\phi_{\mathrm{A}}}{(1-\gamma_s^{\mathrm{A}})\phi_{\mathrm{A}} + (1-\gamma_s^{\mathrm{B}})\phi_{\mathrm{B}}} \tag{12}$$

$$p_{\mathrm{BA}} = \frac{(1-\gamma_s^{\mathrm{A}})(1-\gamma_s^{\mathrm{B}})\phi_{\mathrm{B}}}{(1-\gamma_s^{\mathrm{A}})\phi_{\mathrm{A}} + (1-\gamma_s^{\mathrm{B}})\phi_{\mathrm{B}}} \tag{13}$$

This is not so for polymer solutions or polymer−diluent mixtures, where there are no self-contacts for the low molecular weight components. Again using the subscripts A and B to designate polymer and solvent, respectively, it is a matter of simple algebra to show that

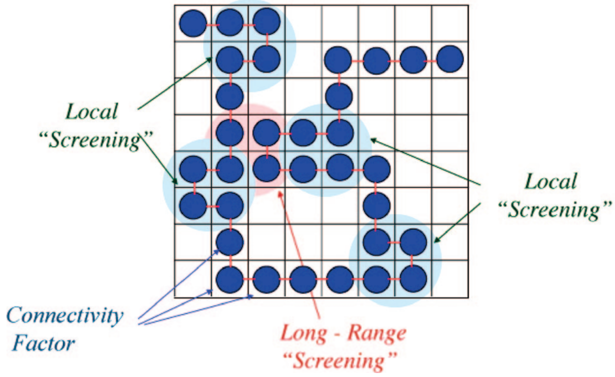

Figure 1. Schematic diagram of a chain on a lattice showing local and long-range contacts or "screening" effects.

$$p_{\mathrm{AA}} = \gamma_s + \frac{(1-\gamma_s)^2\theta_{\mathrm{A}}}{(1-\gamma_s\theta_{\mathrm{A}})} = \gamma_s + \frac{(1-\gamma_s)(1-\gamma)\phi_{\mathrm{A}}}{(1-\gamma\phi_{\mathrm{A}})} \tag{14}$$

where, as in previous work,[16,17] we simplified the equations by defining

$$(1-\gamma) = (1-\gamma_s)(1-\gamma_l) \tag{15}$$

The $(1-\gamma)$ term thus accounts for loss of external (noncovalent) contacts due to both covalent connectivity and conformational effects. (Because there are no connectivity effects in solvent molecules, the superscripts on the γ terms have been omitted.) The probability of a solvent molecule being adjacent to a polymer segment, p_{BA} is then given by:

$$p_{\mathrm{BA}} = \frac{(1-\gamma_s)\phi_{\mathrm{B}}}{(1-\gamma\phi_{\mathrm{A}})} \tag{16}$$

The equivalent probabilities for solvent/solvent contacts and solvent polymer contacts are as follows:

$$p_{\mathrm{BB}} = \frac{\phi_{\mathrm{B}}}{(1-\gamma\phi_{\mathrm{A}})} \tag{17}$$

$$p_{\mathrm{AB}} = \frac{(1-\gamma)\phi_{\mathrm{A}}}{(1-\gamma\phi_{\mathrm{A}})} \tag{18}$$

Note that solvent/solvent contacts are affected by polymer self-contacts, because there is a depletion of polymer segments that are available as neighbors relative to their overall concentration. This is a point made by Lipson and Milner,[9] as we will discuss below. (Note also that eq 17 results in an interesting composition dependence of χ when polymer/solvent interactions are being studied.[17])

When we first started thinking about the problems presented by our results on hydrogen bonded systems, we were skeptical that intrachain noncovalent self-contacts, γ_s, would have an appreciable effect. However, one has to recall that every time a chain comes in contact with itself, two surface sites become unavailable for other contacts. In addition, the results of simulations of chains placed on a cubic lattice gave values of γ_s that varied with the degree of polymerization, m, in the following fashion:[16]

$$\gamma_s = a - \frac{b}{m^{0.5}} \tag{19}$$

The quantities a and b are constants that depend on the system under consideration. The results of this work are reproduced in Figure 2, where for high molecular weight chains values of γ_s in the range 0.30−0.39 were determined. (Values of γ_s for isolated swollen chains were determined to be of the order of 0.1). Also shown on this figure as an insert are results obtained by calculating γ_s using data from polystyrene/cyclohexane solutions near the Θ-temperature.[17] These values were obtained by assuming value of $\gamma_l = 0.22$ (i.e., a lattice coordination number of 9), and calculating γ_s by a fit to critical point data,[17] Values of γ_s between 0.25 and 0.30 were obtained, consistent with simulations, given the difference in lattice coordination number.[16] Furthermore, it was pointed out to us by one of the reviewers of this paper that Wang et al.[27] also accounted for intramolecular contacts in polymer blends and derived equations that are essentially identical to ours (their derivation is far more rigorous, we might add). These authors also calculated the fraction of intramolecular contacts for chains of different lengths, obtaining results that are consistent with those we obtained. Finally, experimental infrared spectroscopic studies of carefully chosen blend systems, where we could count the number of hydrogen bonds (hence contacts), also gave values of γ_s in the range about 0.25 and 0.30.[16,18,19] As might be expected, self-contacts determined spectroscopically for segments in the

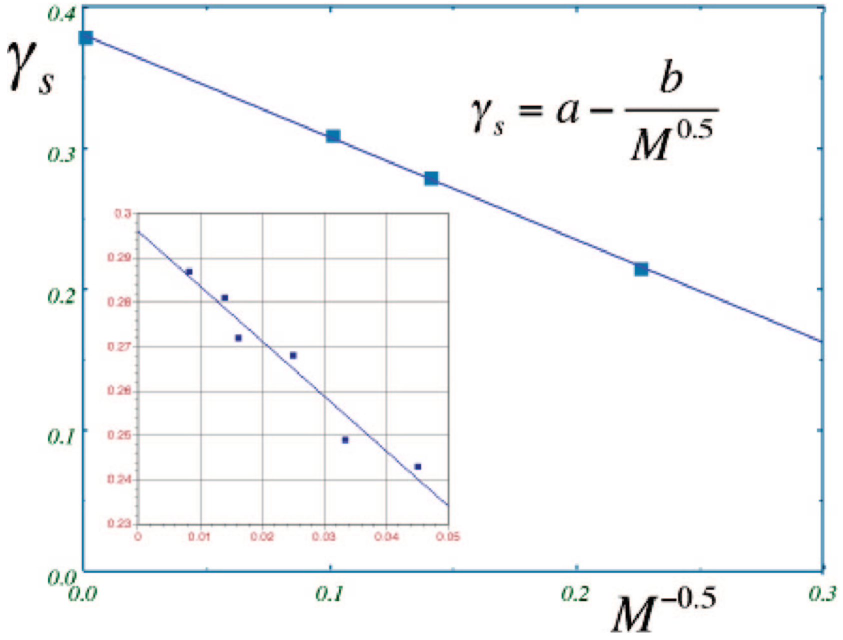

Figure 2. Plot of the calculated fraction of intramolecular (self) contacts, γs, vs $M^{-0.5}$, where M is the degree of polymerization (results from reference [16]). The parameters a and b are constants. Insert: Plot of the fraction of intramolecular (self) contacts, γs, vs $M^{-0.5}$ calculated from critical point data for polystyrene/cyclohexane solutions (data from ref 17).

interior of hyperbranched polymers were far higher, with values of γ_s of the order of $0.70 - 0.80$.[25,26]

The Relationship to Self-Concentration

Lipson and Milner[9] observed that the original form of the Lodge–McLeish model is not self-consistent and should be replaced with:

$$\varphi^{A}_{eff} = \phi^{A}_{self} + \frac{(1-\phi^{A}_{self})^2\phi_{A}}{(1-\phi^{A}_{self})\phi_{A} + (1-\phi^{B}_{self})\phi_{B}} \tag{20}$$

for the A component of a polymer blend or solution (with $\phi^{B}_{self} = 0$ for the latter, if the B component of the mixture is the solvent). This reduces to the original Lodge–McLeish model when $\phi^{A}_{self} = \phi^{B}_{self}$. This has the same form as eq 10 or eq 12, describing the probability of noncovalent contacts, but the latter has to be modified to also include covalently linked neighbors when dealing with the composition dependence of the T_g. As above, this can be accomplished by noting that the fraction of neighbors that are covalently bonded to a chosen A segment in a linear chain is $2/z \approx \gamma^{A}_{l}$ and the remaining $1 - \gamma^{A}_{l}$ fraction of sites will be occupied by p_{AA} A segments. The effective concentration of A segments is then given by

$$\phi^{A}_{eff} = \gamma^{A}_{l} + (1-\gamma^{A}_{l})\left[\gamma^{A}_{s} + \frac{(1-\gamma^{A}_{s})^2\theta_{A}}{(1-\gamma^{A}_{s})\theta_{A} + (1-\gamma^{B}_{s})\theta_{B}}\right] \tag{21}$$

For a polymer blend we can substitute θ_A from eq 7 and using the parameter γ defined in eq 15 to combine γ_l and γ_s, we get:

$$\phi^{A}_{eff} = \gamma^{A} + \frac{(1-\gamma^{A})^2\phi_{A}}{(1-\gamma^{A})\phi_{A} + (1-\gamma^{B})\phi_{B}} = \phi^{A}_{self} + \frac{(1-\phi^{A}_{self})^2\phi_{A}}{(1-\phi^{A}_{self})\phi_{A} + (1-\phi^{A}_{self})\phi_{B}} \tag{22}$$

where it can be seen that the result is the same as the self-consistent form of the Lodge–McLeish equation if $\gamma^{A} = \phi^{A}_{self}$ and $\gamma^{B} = \phi^{B}_{self}$.

For polymer/diluent mixtures, equivalent adjustments to the equations describing the external contacts of the polymer also have to be made so as to include covalently bonded neighbors. The equation for the local concentration of the polymer becomes

$$\phi^{A}_{eff} = \gamma^{A} + \frac{(1-\gamma^{A})^2\phi_{A}}{(1-\gamma^{A}\phi_{A})} = \phi^{A}_{self} + \frac{(1-\phi^{A}_{self})^2\phi_{A}}{(1-\phi^{A}_{self}\phi_{A})} \tag{23}$$

while the effective concentration of the solvent is given by:

$$\phi^{B}_{eff} = \frac{\phi_{B}}{(1-\gamma^{A}\phi_{A})} = \frac{\phi_{B}}{(1-\phi^{A}_{self}\phi_{A})} \tag{24}$$

The self-contact relationships discussed here involve only nearest neighbor contacts and self-concentration effects could well involve a larger local volume. However, as the work of Lipson and Milner[9] has demonstrated, it is the immediate neighbors to a segment that show the largest self-concentration effect. In the calculations presented below, we will therefore assume that self-concentration depends on both connectivity and conformational effects according to the equations presented above and following eq 15 argue that ϕ_{self} can be defined in terms of two components, a covalent connectivity term, ϕ^{cov}_{self} ($= \gamma_l$) and a conformational connectivity term, ϕ^{conf}_{self} ($=\gamma_s$), with

$$(1-\phi_{self}) = (1-\phi^{cov}_{self})(1-\phi^{conf}_{self}) \tag{25}$$

or

$$\phi_{self} = \phi^{cov}_{self} + (1-\phi^{cov}_{self})\phi^{conf}_{self} \tag{26}$$

The advantage of this division into two components is that we know that ϕ^{cov}_{self} should be of the order of 0.20, while for polymers such as polystyrene values of $\gamma_s = \phi^{conf}_{self} \sim 0.24-0.30$ for unperturbed chains have been determined,[17] allowing a test of the model within this range of values. In addition, this approach predicts that the same polymer will have different values of ϕ_{self} in mixtures where the chain conformation is relatively unperturbed compared to situations where the chain is swollen and hence has smaller values of ϕ^{conf}_{self}. Before getting to calculations based on these definitions, however, we will first consider the equations we will use to describe the composition dependence of the T_g.

The Composition Dependence of the Glass Transition Temperature

In much of the work that has utilized the self-concentration approach, the composition dependence of a mixture has been described in terms of the Fox equation:[28]

$$\frac{1}{T_g^{mix}} = \frac{w_A}{T_g^A} + \frac{w_B}{T_g^B} \tag{27}$$

where T_g^{mix} is the glass transition temperature of the mixture, T_g^A and T_g^B are the pure component T_gs and w_A and w_B are weight fractions.

The Fox equation is an approximation and can be obtained from an equation due to Couchman and Karasz[29] and Couchman[30] that assumes that pure component entropies and the entropy of mixing are continuous at the glass transition. The following equation is obtained if it is assumed that differences in the entropy of mixing in the glassy and liquid states are negligible:

$$\ln T_g^{mix} = \frac{w_A \Delta C_p^A \ln T_g^A + w_B \Delta C_p^B \ln T_g^B}{w_A \Delta C_p^A + w_B \Delta C_p^B} \tag{28}$$

where ΔC_p^A and ΔC_p^B are the specific heat increments of the components at the T_g. If the T_gs of the polymers are not too different and if it assumed that $\Delta C_p^i T_g^i \approx$ constant, then the Fox equation is obtained. Although there are some problems with this approach,[31] it appears to work well in systems with weak intermolecular interactions and where the difference in the values of the T_gs are not too large (eq 27 also assumes that ΔC_p^i is constant with temperature).

There are numerous other expressions that have been used to model the composition dependence of the T_gs. We will mention only one other, that developed by Kwei[32] to model systems with specific interactions, which show significant deviations from the predictions of the Fox equation and Couchman's equation. It has also been widely applied to other mixtures that cannot be described by the Fox equation. The Kwei equation has the following form:

$$T_g^{mix} = \frac{w_A T_g^A + k w_B T_g^B}{w_A + k w_B} + w_A w_B q \tag{29}$$

where k and q are parameters that can be fit to the data, with q accounting for specific interactions. Assuming that the enthalpy of mixing is continuous at the glass transition, we previously obtained a complicated equation for hydrogen-bonded systems that reduced to the Kwei equation, with $k = \Delta C_p^B / \Delta C_p^A$ and q a function of the enthalpy of mixing.[33]

In order to account for self-concentration in calculating the composition dependence of the T_g, the weight fractions (w_A and w_B) in the above equations are replaced with the effective local weight fractions of each component, calculated from the appropriate equations given in the preceding section. (In using the Kwei equation, one then has to be careful of the definition of the A and B components in calculating the parameter k.)

Calculations of the Composition Dependence of T_g: Polymer Blends

Over the years, a number of studies have reported anomalies in the composition dependence of the T_gs of various polymer mixtures, particularly those where the T_gs of the components differed significantly. Instead of a single curve, discontinuities or cusps were observed, separating two sections of different curvature. The T_gs measured in the region of the cusp were usually extremely broad and Beirnes and Burns[34] observed more than twenty years ago that in poly(vinyl chloride)/dioctyl phthalate (PVC/DOP) blends two T_gs could be distinguished in the composition range of the discontinuity, although they reported the data as an average of these values. We will consider polymer/diluent systems in the following section, but here we will only consider the data reported by Gaikwad et al.[13] Three blends were studied by these authors, poly(ethylene oxide)/poly(lactide) (PEO/PLA), PEO/poly(vinyl acetate) (PEO/PVAc) and an end-group methylated PEO, poly(ethylene oxide)−dimethyl ether, (PEO−DME) mixed with poly(methyl methacrylate) (PMMA). A good fit of plots of T_g vs composition was obtained using the Lodge−McLeish model, but the value of ϕ_{self} for PEO varied from 0.27 to 0.64. Our purpose in this section is to show that using the Lodge−McLeish equation or the Lipson−Milner self-consistent form, eqs 21 or 26, the data can be fit with self-concentration terms that are consistent with a fraction of self-contacts that are of the order of 0.4 ($\phi_{self}^{cov} \approx 0.20$, $\phi_{self}^{conf} \approx 0.25$).

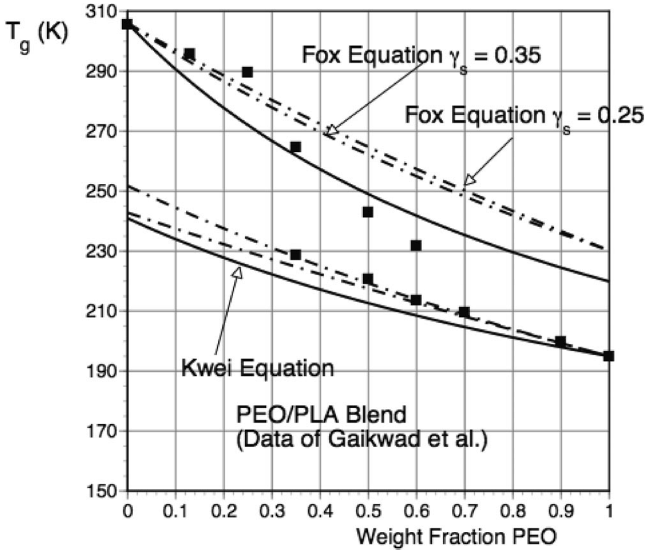

Figure 3. Plot of the composition dependence of the T_g for PEO/PLA blends. The data points are from reference.[13] The dash-dot curves were calculated using the Fox equation, assuming $\phi_{self}^{cov} = 0.20$ and $\gamma_s(\mathrm{PLA}) = \phi_{self}^{conf}(\mathrm{PLA}) = 0.25$ (i.e., $\phi_{self} = 0.40$). Two sets of parameters were assumed for the PEO components, $\phi_{self}^{conf}(\mathrm{PEO}) = 0.25$, and $\phi_{self}^{conf}(\mathrm{PEO}) = 0.35$. The solid-line curve was calculated using the Kwei equation ($q = 0$) with $\gamma_s = \phi_{self}^{conf} = 0.25$ for both polymers.

The T_gs of PEO/PLA blends obtained by Gaikwad et al. are plotted as a function of composition in Figure 3. Also shown on this figure are three curves obtained using the self-consistent form of the Lodge−McLeish model (eq 20) and the definition of ϕ_{self} as the sum of covalent and conformational components (eq 26). Two of the curves use the Fox equation. For one curve, we assumed that the fraction of self-contacts, γ_s, or ϕ_{self}^{conf} is the same for each polymer with a value of 0.25 (i.e., the Lodge−McLeish model), while for the second curve we assumed a value of 0.35 for PEO, but maintained a value of ϕ_{self}^{conf} equal to 0.25 for PLA. Essentially, for the latter curve we assumed that the highly flexible nature of PEO results in a larger fraction of self-contacts, even in low molecular weight samples. Values of $\phi_{self}^{cov} = 0.20$ were assumed, corresponding to a coordination number of 10. In effect, values of ϕ_{self} equal to 0.40 and 0.48, respectively, were used in the calculations. It can be seen that there are very small difference between the curves calculated for PLA in its local environment, and somewhat larger differences for PEO in its local environment, with the curve calculated using γ_s equal to 0.35 giving a better fit to the PEO data. Neither gives a particularly good fit to the PLA data, however. Also shown in Figure 3 is the curve obtained using the Kwei equation with ϕ_{self}^{conf} values of 0.25 (PLA) and 0.25 (PEO) (i.e., the Lodge−McLeish model). The value

Table 1[a]

polymer or diluent	density (g/cm^3)	T_g (K)	ΔC_p (J/[g K])	$T_g\Delta C_p$ (J/g)
PEO	1.14	195	1.295	252
PEO−DME	assumed = PEO	178	0.082	14.6
PMMA	1.17	393	0.316	124
PLA	1.248	306	0.56	171
PVAc	1.19	291	0.55	160
PS	1.05	378	0.28	107
TCP	1.16	221	0.48	105
toluene	0.87	117	0.625	73
DBP	1.05	182	0.54	113
DMP	1.19	194	0.5	97

[a] Data from refs 11, 13, 14, 31, and 35.

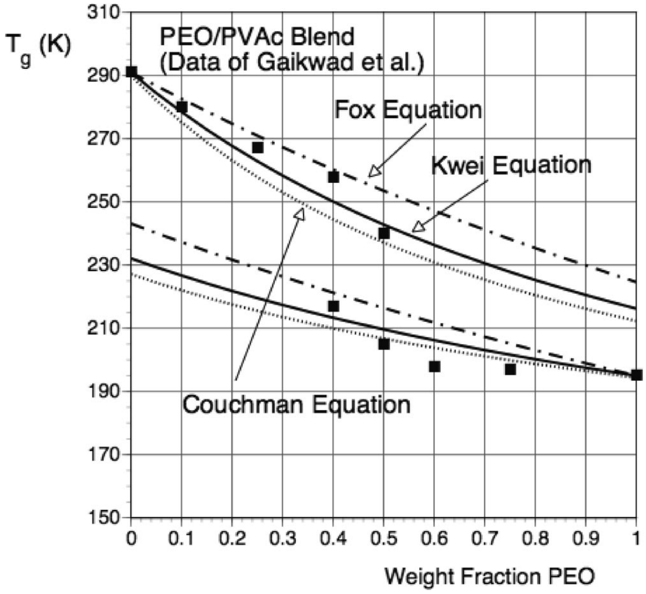

Figure 4. Plot of the composition dependence of the T_g of PEO/PVAc blends. The data points are from reference.[13] The solid-line curves were calculated using the Kwei equation ($q = 0$). The dash-dot curves were calculated using the Fox equation. The dotted-line curves were calculated using Couchman's equation. It was assumed that $\phi_{self}^{cov} = 0.20$ and $\gamma_s = \phi_{self}^{conf} = 0.25$ ($\phi_{self} = 0.40$) for both polymers.

of k was determined from the specific heat increments listed in Table 1 (being careful to remember what is being defined as the A component and the B component in each calculation). The value of q was put equal to zero. Taken as a group, the calculated curves largely bracket the data. Given the assumptions that have gone into both the self-contact and T_g/composition models, together with errors inherent in measuring a broad transition like the T_g, further refinement of the calculations (e.g., to obtain a best fit value of ϕ_{self} or fit to the Kwei equation by adjusting the value of q) would appear to be pointless.

Figure 4 shows the results obtained from the PEO/PVAc system. We assumed ϕ_{self} values of 0.4, for each polymer (i.e., $\phi_{self}^{cov} = 0.20$, $\phi_{self}^{conf} = 0.25$), but calculated three curves, using the Fox equation, Couchman's equation and the Kwei equation (with k again calculated from the specific heat increments listed in Table 1 and $q = 0$). The curves essentially bracket most of the data. A better fit to the Fox equation can be obtained if the value of ϕ_{self}^{conf} for the polymers is assumed to be a little larger than 0.25 and a very good fit to the Kwei equation can be obtained by adjusting q, but again the precision of the data and the limitations of the models do not justify making any major effort to obtain a best fit. What is more important is that with reasonable assumptions about the value of ϕ_{self} an acceptable fit to the data is obtained.

The final blend considered here, PEO−DME/PMMA gave us a problem in terms of using both the Couchman and Kwei equations. This is because of the very small value of ΔC_p reported by Gaikwad et al.[13] For many materials $\Delta C_pT_g \approx$ constant, although there is often considerable variation and this is reflected in Table 1. Nevertheless, values of the order of 100 J/g or more are obtained for most systems. The value of ΔC_pT_g for PEO−DME was found to be 14.6 J/g, resulting in strange looking curves when Couchman's equation is used. However, if we use the value of ΔC_p reported for PEO, the curve shown in Figure 5 is obtained, where it can be compared to the results obtained using the Kwei equation (k was determined from the data in table 1, $q = 0$). The calculated curves essentially bracket the experimental data for both components (values of $\phi_{self}^{cov} = 0.20$,$\phi_{self}^{conf} = 0.25$ were again assumed). Gaikwad et al.[13] also plotted data for the PEO/PMMA system, but did not tabulate the data. We estimated these from the plot (no doubt imperfectly) and obtained results essentially identical to those shown in Figure 5, with the calculated curves bracketing the experimental data.

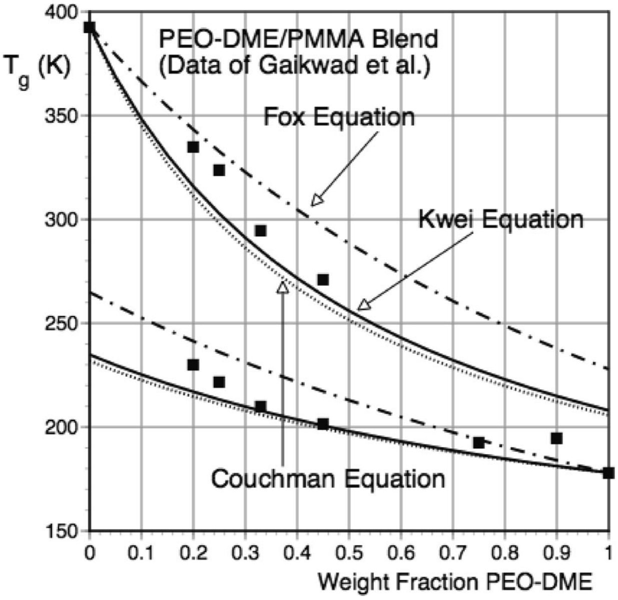

Figure 5. Plot of the composition dependence of the T_g of PEO−DME/PMMA blends. The data points are from reference.[13] The solid-line curves were calculated using the Kwei equation ($q = 0$). The dash-dot curves were calculated using the Fox equation. The dotted-line curves were calculated using Couchman's equation. It was assumed that $\phi_{self}^{cov} = 0.20$ and $\gamma_s = \phi_{self}^{conf} = 0.25$ ($\phi_{self} = 0.40$) for both polymers.

To summarize, if self-concentration is considered to be the result of two factors, the first a consequence of covalent connectivity while the second a result of conformational effects, a good agreement between calculated and observed T_gs can be obtained using the Lodge−McLeish model. In previous work, very different values of ϕ_{self} for the same polymer were used to fit data in different blends. This appears to be more a result of the limitations of the Fox equation than the Lodge−McLeish model. Using other models for the composition dependence of the T_g, the values of the self-concentration term can be kept the same for a particular polymer in different mixtures. In addition, the contribution of the conformational component, $\phi_{self}^{conf} \sim 0.25$ or so, is consistent with values of self-contacts obtained in previous work.

Calculations of the Composition Dependence of T_g: Polymer/Diluent Systems

The original form of the Lodge−McLeish model does not result in a self-concentration effect for the low molecular weight component of polymer/diluent mixtures, because of the absence of self-contacts in the latter. However, two T_gs have been observed in a number of studies of apparently miscible systems of this type. For example, Savin et al.[11] reported data for polystyrene/phthalate diluent systems that in terms of general trends closely resembled data from polymer blends—two lines of different curvature with two T_gs detected in the midcomposition range. The data for PS/DBP (di-*n*-butyl phthalate) mixtures was discussed at some length by Lipson and Milner,[9] who observed that the T_g of the polystyrene (PS) rich component could only be modeled if small values of ϕ_{self} (less than 0.1) were assumed. This is in contrast to values of the order of 0.35 determined by Lutz et al.[4] for PS containing mixtures where the difference in the T_gs of the two components is more than about 20 K. This is also much smaller than a value of the order of 0.4 that would be expected on the basis of the arguments made above and a value of 0.27 based on the Kuhn segment length.[10] Furthermore, although Lipson and Milner pointed out that a self-consistent form of the Lodge−McLeish model should be used to model the composition dependence of the T_g (eq 20), which would lead to a depletion of PS segments adjacent to solvent molecules, they found that a value of $\phi_{self} = 0.42$ was required to fit the DBP component T_g, very different from the value of less than 0.1 required to fit the PS data. Here we will show that values of ϕ_{self} consistent with values of ϕ_{self}^{conf} obtained from experimental work and simulations give a good fit to the data. There is a complication, however, involving the swelling of polymer chains in good solvents.

One consequence of dividing ϕ_{self} into a covalent connectivity component and a conformational component is that the latter will depend on chain conformation. This does not come into play in the study of blends with relatively weak interactions in the concentrated regime, discussed in the preceding section, as neutron scattering studies have shown that chain conformations are essentially unperturbed in such mixtures.[35] Polymer solutions behave differently, however. In good solvents, the radius of gyration increases continuously with decreasing concentration from the value found under theta conditions to the characteristic value found in dilute solutions.[36,37] One would expect that the fraction of self-or same-chain noncovalent contacts ($\gamma_s = \phi_{self}^{conf}$) should also decrease. Simulations of polymer chains on a cubic lattice have shown that self-contacts decreases from values of about 0.38 for a high molecular weight polymer chain in the melt to a value close to 0.1 for a chain following self-avoiding walk statistics.[16,38] On the other hand, in theta or poor solvents, one would anticipate that the fraction of self-contact terms for a particular polymer chain should be close in value to those found in blends. Fortunately, data describing the composition dependence of the T_g in polymers mixed with both good and poor solvents is available to test these ideas.

We will start by considering mixtures of polystyrene (PS) with various phthalates using the data reported by Savin et al.[11] These authors pointed out that the composition dependence of the T_gs of these mixtures appeared like a polymer blend system rather than a polymer/solvent mixture. We suggest that this is because Dioctyl phthalate (DOP) is a theta solvent for polystyrene (at 22 °C),[39] while dimethyl phthalate (DMP) and dibutyl phthalate are considered to be poor solvents.[40] We have shown in previous work that the fraction of noncovalent self-contacts of polystyrene chains in theta solutions is about 0.25,[17] suggesting that we use the value of $\phi_{self} = 0.4$ (corresponding to $\phi_{self}^{cov} = 0.20, \phi_{self}^{conf} = 0.25$) utilized to model the composition dependence of the T_g of blends, described in the preceding section. Figure 6 shows the results obtained for PS/DOP mixtures using the Lipson−Milner self-consistent form of the Lodge−McLeish equations (eqs 23 and 24) and these parameters. There are two curves shown on this figure, one obtained using the Fox equation, while the other utilized the Kwei equation with the parameter $q = -75$ and values of k calculated from specific heat increments (Table 1). The latter gives a very good fit too the data, while the fit obtained using the Fox equation is poor. One should always get a better fit using an equation with an adjustable parameter, of course, but we think there is more to it than that. If we now assume the same values of $q = -75$ and $\phi_{self} = 0.4$ used for PS/DOP and apply them to PS/DBP and PS/DMP mixtures, we again get a very good fit to the data, as shown in Figures 7 and 8. (Again, values of k from were calculated from specific heat increments.)

The q parameter in the Kwei equation was originally introduced to account for specific interactions. In this regard, the phthalates are known to associate in solution, presumably

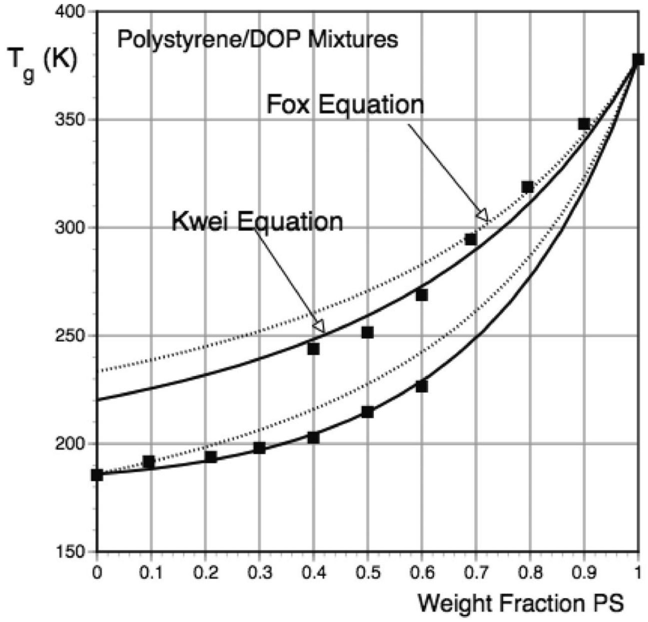

Figure 6. Plot of the composition dependence of the T_g of PS/DOP mixtures. The data points are from ref 11. The solid-line curves were calculated using $\phi_{self}^{cov} = 0.20$ and $\gamma_s = \phi_{self}^{conf} = 0.25$ ($\phi_{self} = 0.40$) for polystyrene and the Kwei equation ($q = -75$). The dotted-line curves are calculated using the Fox equation.

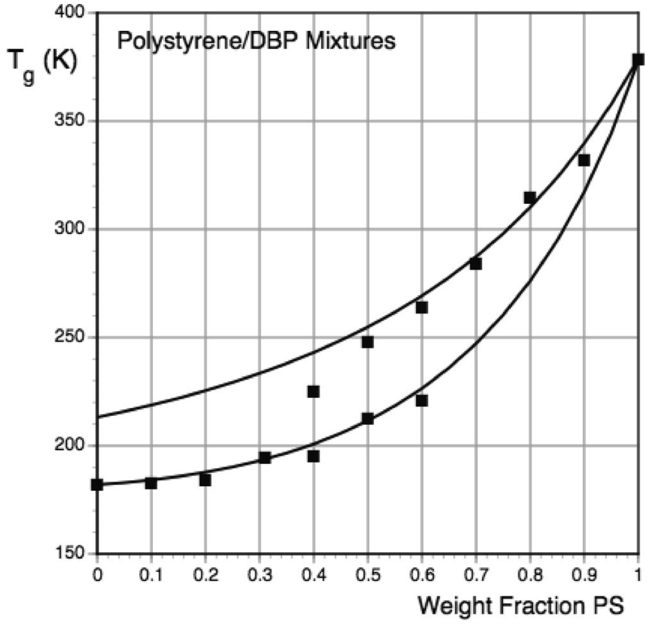

Figure 7. Plot of the composition dependence of the T_g of PS/DBP mixtures. The data points are from reference.[11] The solid-line curves were calculated using $\phi_{self}^{cov} = 0.20$ and $\gamma_s = \phi_{self}^{conf} = 0.25$ ($\phi_{self} = 0.40$) for polystyrene and the Kwei equation ($q = -75$).

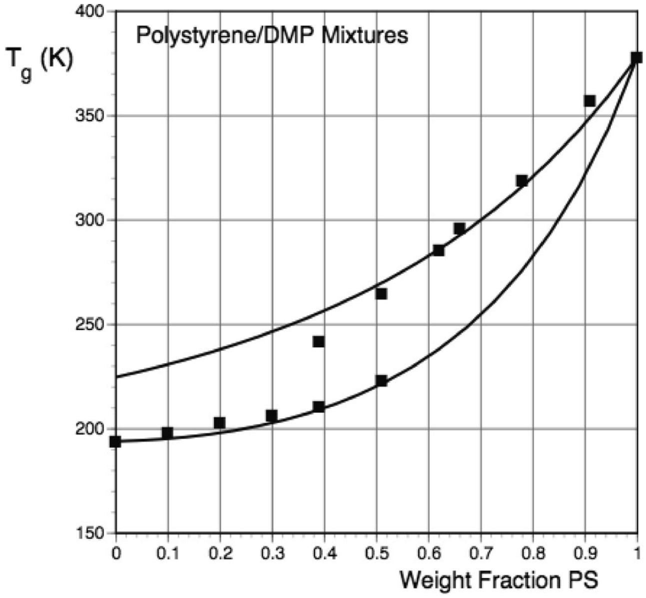

Figure 8. Plot of the composition dependence of the T_g of PS/DMP mixtures. The data points are from reference.[11] The solid-line curves were calculated using $\phi_{self}^{cov} = 0.20$ and $\gamma_s = \phi_{self}^{conf} = 0.25$ ($\phi_{self} = 0.40$) for polystyrene and the Kwei equation ($q = -75$).

as a result of dipole attractions between the ester groups,[41] so that a nonzero value of q would seem to be justified for these systems. There are other factors that could come into play, however. For example, free volume differences between polymers are relatively small compared to those between polymers and solvents. Such differences affect excess entropy terms in polymer/diluent mixtures and the Kwei equation may be empirically accounting for these factors. In this regard, nonzero values of the Kwei q parameter were found by Zheng and Simon[6] for mixtures of poly(α-methyl styrene) (PαMS) with one of its oligomers, data we will consider below.

We will now turn to polymers in good solvents, such as polystyrene in toluene. Many years ago, Braun and Kovacs[42] reported measured the T_gs of these mixtures and observed that there was a cusp in plots of the composition dependence. More recent results obtained by Taniguchi et al.[14] revealed the presence of two distinguishable T_gs, as shown in Figure 9. The curves shown in this figure were calculated two ways. Both used the Kwei equation with $q = -75$ and values of k calculated from specific heat increments, to be consistent with the PS/phthalate mixtures described above. The dash-dot curves were calculated using parameters characteristic of polymers in theta solvents, or polymer blends, with $\phi_{self}^{cov} = 0.20$ and $\gamma_s = \phi_{self}^{conf} = 0.25$ ($\phi_{self} = 0.40$) for PS. The solid-line curves were calculated using $\phi_{self}^{cov} = 0.20$ and $\gamma_s = \phi_{self}^{conf} = 0.08$ ($\phi_{self} = 0.26$). The latter value used for ϕ_{self}^{conf} is based on the assumption that the chain is expanded and the fraction of noncovalent contacts approaches that characteristic of polymers in dilute solutions. For chains on a cubic lattice, this value is ~0.1,[16,38] so one would expect values somewhat smaller than this on a lattice with a larger coordination number. We assumed a value 0.08. Neutron scattering results show that the PS chains in good solvents are considerably expanded even at volume fractions as high as 0.2−0.3,[36,37] so one would expect the data to interpolate between these two curves as a function of increasing PS concentration. Certainly, at low concentrations the assumption of an expanded chain gives a better fit, but because the curves converge to the value of the T_g of PS at high polymer concentrations, both curves give a reasonable fit to this part of the data.

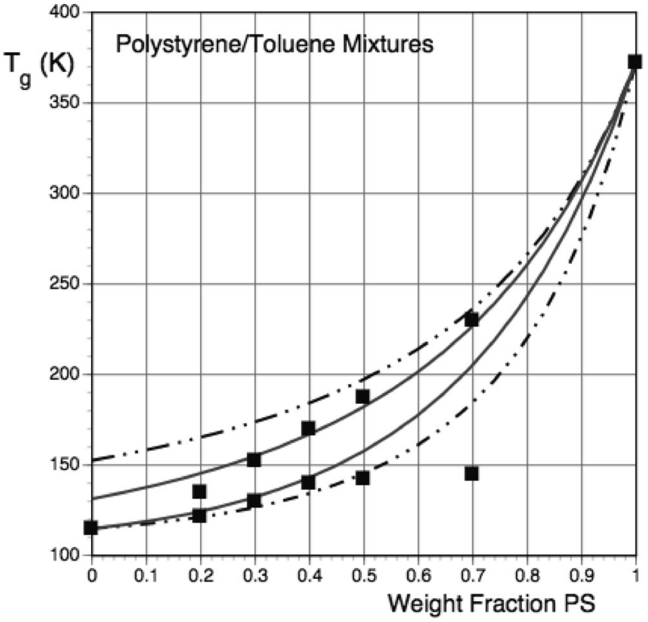

Figure 9. Plot of the composition dependence of the T_g of polystyrene/toluene mixtures. The data points are from reference.[14] The dash-dot curves were calculated using $\phi_{self}^{cov} = 0.20$ and $\gamma_s = \phi_{self}^{conf} = 0.25$ ($\phi_{self} = 0.40$) for polystyrene and the Kwei equation ($q = -75$). The solid-line curves were calculated using $\phi_{self}^{cov} = 0.20$ and $\gamma_s = \phi_{self}^{conf} = 0.08$ ($\phi_{self} = 0.26$) for polystyrene and the Kwei equation ($q = -75$).

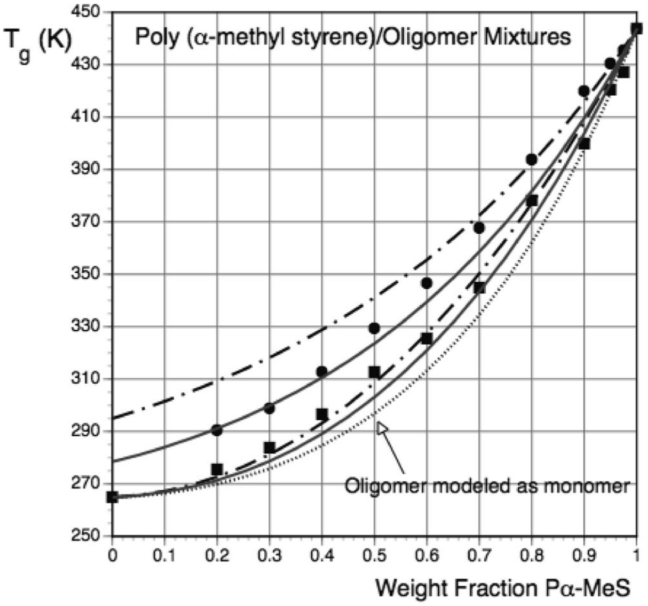

Figure 10. Plot of the composition dependence of the T_g of PαMS/oligomer mixtures. The data points are from reference.[6] The dash-dot curves were calculated using $\phi_{self}^{cov} = 0.20$ and $\gamma_s = \phi_{self}^{conf} = 0.25$ for polystyrene, $\phi_{self}^{cov} = 0.16$ for the oligomer, together with the Kwei equation ($q = -130$). The solid-line curves were calculated using $\phi_{self}^{cov} = 0.20$ and $\gamma_s = \phi_{self}^{conf} = 0.08$ ($\phi_{self} = 0.26$) for polystyrene, $\phi_{self}^{cov} = 0.16$ for the oligomer, and the Kwei equation ($q = -130$).

As mentioned above, nonzero values of the Kwei q parameter were found by Zheng and Simon[6] for mixtures of poly(α-methyl styrene) (PαMS) with one of its oligomers. These authors observed two T_gs in mixtures of this polymer with a 5-*mer*. Their data is shown in Figure 10. They first determined that the Fox equation did not fit plots of the average T_gs of the mixtures and therefore used the Kwei equation. Values of $k = 1$ and $q = -130$ were determined. These parameters were then used to calculate the T_gs characteristic of the local compositions of each component using the Lodge−McLeish model. Values of ϕ_{self} equal to 0.22, an estimate based on the Kuhn segment length, could not fit the experimental results. Very small values of ϕ_{self} (0.056) were required to obtain a correspondence between calculated and observed values of the T_gs, similar to what was found for the local composition of PS in PS/DOP mixtures by Lipson and Milner.[9] Using the self-consistent model, we calculated two curves, each using the Kwei model with $q = -130$ and values of k from specific heat increments estimated from plots reported by these authors ($k = 1.28$ for the self-concentration of polymer and $k = 0.78$ for the self-concentration of oligomer). As with PS solutions in toluene, dash-dot curves were calculated using parameters characteristic of polymers in Θ solvents, or polymer blends, with $\phi_{self}^{cov} = 0.20$ and $\gamma_s = \phi_{self}^{conf} = 0.25$ ($\phi_{self} = 0.40$) for PS. The solid-line curves were calculated using $\phi_{self}^{cov} = 0.20$ and $\gamma_s = \phi_{self}^{conf} = 0.08$ ($\phi_{self} = 0.26$) for the polymer. However, the oligomer (5-mer) has a self-concentration term, $\phi_{self} = \phi_{self}^{cov} = 0.16$ calculated from eq 4, where we assume that the oligomer is too short to give a conformational contribution to ϕ_{self}. Using the self-consistent form of the Lodge–McLeish model, we get a good agreement between the model and experiment, with the data points interpolating nicely between the assumption of an expanded chain at low polymer concentrations and a chain with unperturbed dimensions at higher concentrations.

Also shown in Figure 10 is the curve calculated for the oligomer as if it were a monomer. Given the presumed errors in the models and the precision of determining the midpoint of a broad transition like the T_g, one cannot make too much of this, however. The main point is that if self-concentration is considered to be the result of two factors, the first a consequence of covalent connectivity while the second a result of conformational effects, a good agreement between calculated and observed T_gs for polymer/diluent systems can be obtained using the Lipson–Milner self-consistent form of the Lodge–McLeish model.

Conclusions and Ramifications

Chain connectivity can affect self-concentration in two ways: First, there is what we have called a covalent connectivity effect, which manifests itself in the probability that a site adjacent to a chosen segment on a chain is occupied by a like or unlike segment; second, there is a conformational connectivity effect that is a consequence of a chain bending back on itself through both local and long-range factors that will depend on the flexibility of the chain. If the covalent connectivity effect is treated using a lattice model, then in calculating the average properties of polymer blends there is a cancelation of terms and there is no contribution to self-concentration from noncovalent contacts. In addition, chain connectivity effects, as modeled by Guggenheim statistics, for example, do not predict an enhanced self-concentration in materials like dendrimers and hyperbranched polymers.

Self-concentration effects in polymer blends appear to be modeled very well by the Lodge–McLeish model[10] if one takes into account the limitations of models used to calculate the composition dependence of the T_g. If one considers ϕ_{self} to be a consequence of both covalent and conformational effects there would appear to be lower and upper limits to ϕ_{self} set by values ϕ_{self}^{cov} ($= \gamma_l \sim 0.2$) and ϕ_{self}^{conf} ($=\gamma_s \sim 0.24-0.35$), such that for most system ϕ_{self} would lie in the range 0.40 to 0.48. (Stiff or swollen chains would have smaller values.)

In contrast to polymer blends, self-concentration in polymer/diluent mixtures depends on conformational connectivity effects in a more complex manner that is related to solvent “quality”. The fraction of noncovalent same-chain contacts, a measure of the contribution of conformational connectivity used in the calculations reported here, was of the order of 0.25 for polymer blends and polymers in poor or theta solvents. This value is consistent with previous experimental determinations of this parameter and the results of simulations.[16,17,19] Smaller values of self-contacts, of the order of 0.05–0.01, would be expected for swollen chains[16,38] and this assumption gives good results for polymers in good solvents. The calculated composition dependence of the T_g also depends strongly on whether one chooses the Fox equation, the Couchman equation or the Kwei equation to describe the variation of T_g with composition.

The self-contact parameter, $\gamma_s = \phi_{self}^{conf}$, depends on both short-range and long-range conformational effects and should therefore also be related to factors such as chain stiffness, chain architecture and molecular weight. However, the dependence on molecular weight will be difficult to probe experimentally. The previously developed and experimentally confirmed relationship of γ_s to molecular weight only applies to chains that are of sufficient length to allow long-range effects. Using data from previous work on polystyrene solutions, this suggests that γ_s will have values ranging from about 0.19 to about 0.30 for this polymer.[17] Such variations will be difficult to distinguish, given the breadth of observed blend T_gs and the limitations of models describing the composition dependence of T_g.

The variation with chain architecture should be a different matter. Values of the self-contact parameter, $\gamma_s = \phi_{self}^{conf}$of about $0.7 - 0.8$ for internal segments of hyperbranched polymers when mixed with linear polymers or solvents have been determined by infrared spectroscopy.[23,24] Measurements of the composition dependence of the glass transition temperature of mixtures of this type should provide a more sensitive test of this approach.

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