$$\sigma_{ij}^3 = (\sigma_{ii}^3 + \sigma_{jj}^3)/2 \qquad \text{(C.23)}$$

Using this rule for σ_{ij} it can be shown that ϵ^* is given by eq 36.

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Compositional Variation of Glass-Transition Temperatures. 2. Application of the Thermodynamic Theory to Compatible Polymer Blends

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ABSTRACT: The characteristic continuity of extensive thermodynamic parameters at glass-transition temperatures forms the basis for a theory to predict T_g in intimate mixtures of compatible high polymers from pure-component properties. A relation derived from the mixed system entropy in terms of pure component heat capacity increments and glass-transition temperatures is shown to arise as a consequence of the connectivity constraint on the excess mixing entropy in these blends. Four known essentially empirical relations for the effect, including a predictive version of the Wood equation, are obtained as special cases of this expression. A second mixing relation is derived in terms of pure component properties from the volume continuity condition at T_g. Quantitative restrictions on excess mixing volumes associated with this relation suggest that the entropic expression may be of wider use. The derivation of relations for the effect of pressure on T_g is touched on. Finally, for two related blends, the entropy-based relation is shown to predict glass-transition temperatures in very good agreement with experimental values.

The prediction of glass-transition temperatures in compatible mixtures from pure-component properties presents a problem of some technological and scientific interest. Plasticized polymers and polymer blends find a wide variety of industrial applications; however, the compositional variation of glass-transition temperatures in these mixtures is generally discussed in terms of essentially empirical expressions.[1] The physically plausible "free volume" hypothesis has provided a rationalization of certain of these relations.[1-4] Separately, a statistical mechanical interpretation of composition effects on T_g has been given in terms of the DiMarzio–Gibbs "configurational" entropy hypothesis of glass formation.[5]

The first of these approaches is known to offer some basic difficulties and can lead to relations which are inconsistent with experimental evidence, while the DiMarzio–Gibbs method does not appear to provide an explicit expression for T_g in terms of composition. A quasi-macroscopic form of the configurational entropy hypothesis of glass formation has been applied recently to the problem in ideal and regular solutions[6] but, necessarily, is couched in terms of fictive rather than actual transition temperatures. Its application to mixtures thus necessitates knowledge of the fusion entropy for each pure component, assumes the compositional variation of fictive transition temperatures to reproduce that of T_g, and re-

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quires the mixed-system crystalline entropy to mimic that of the amorphous mixture below T_g. To consider the latter assumption, if at least one component is macromolecular, geometrical constraints imposed by a lattice could cause mixing behavior in the crystalline and disordered systems to differ considerably. Additionally, correct use of this description necessitates a knowledge of the conformational contribution to transition heat capacity increments, a further problem.[7]

In recent publications, Couchman and Karasz[8,9] have outlined a classical thermodynamic theory of the relation between glass-transition temperatures and composition in compatible binary mixtures. For ideal and regular solutions, two particularly simple equations for the phenomenon may be derived in terms of pure-component properties. A relation formally identical to one of these expressions arises also in the context of the configurational entropy hypothesis of glass formation.[6] The predicted and observed compositional variations of T_g were found to agree fairly well for several binary alcohol systems which conform moderately to ideal or regular solution behavior.[6,9,10] It cannot though be assumed that the formalism for such simple solutions is applicable to compatible polymer systems. It is, therefore, the purpose of this paper to provide an analogous method for predicting the effect of composition on T_g for intimately miscible polymers, in which the influence of specific interactions, the role of connectivity, and so forth need be considered.

Derivation of Formal Relations for the Compositional Variation of T_g in Polymer Systems

Two equations for the effect of mixing on glass-transition temperatures at constant pressure can be derived on the basis of classical thermodynamics. These arise, respectively, from the characteristic continuity of total system entropy and volume at T_g, in conjunction with the use of recognized finite transition discontinuities in their derivatives. Since, generally, the entropy assumes a superior position in thermodynamics the derivation of a mixing relation from this variable is treated in some detail. There are, also, specific reasons which suggest that in polymer systems this relation may find somewhat wider application than an analogous expression obtained from the system volume (see later). For simplicity, the theoretical relations are derived for binary mixtures, but can be generalized to n-component systems with no obvious difficulty.

The pure-component molar entropies are denoted as S_1, S_2 and their respective mole fractions (for polymers it is useful to consider a mole of mers) as X_1, X_2. The mixed system molar entropy, S, can then be defined as

$$S = X_1S_1 + X_2S_2 + \Delta S_m \tag{1}$$

where the excess entropy of mixing, ΔS_m, includes all contributions arising from mixing the two pure components. For later convenience S_1 and S_2 are referred to their respective pure-component glass-transition temperatures T_{g_1} and T_{g_2}, when their values are denoted as S_1^0, S_2^0. At an arbitrary temperature T, use of these definitions and of the pure-component heat capacities C_{p_1}, C_{p_2} leads directly to the expression

$$S = X_1\left\{S_1^0 + \int_{T_{g_1}}^{T} C_{p_1}\,\mathrm{d}\ln T\right\} + X_2\left\{S_2^0 + \int_{T_{g_2}}^{T} C_{p_2}\,\mathrm{d}\ln T\right\} + \Delta S_m \tag{2}$$

The mixed-system glass-transition temperature, T_g, is defined by the requirement that S for the glassy state is identical to that for the liquid state. This condition and use of appropriate superscripts g, l lead to the equation

$$X_1^g\left\{S_1^{0,g} + \int_{T_{g_1}}^{T_g} C_{p_1}^g\,\mathrm{d}\ln T\right\} + X_2^g\left\{S_2^{0,g} + \int_{T_{g_2}}^{T_g} C_{p_2}^g\,\mathrm{d}\ln T\right\} + \Delta S_m^g = X_1^l\left\{S_1^{0,l} + \int_{T_{g_1}}^{T_g} C_{p_1}^l\,\mathrm{d}\ln T\right\} + X_2^l\left\{S_2^{0,l} + \int_{T_{g_2}}^{T_g} C_{p_2}^l\,\mathrm{d}\ln T\right\} + \Delta S_m^l \tag{3}$$

Since the system composition is fixed, $X_i^g = X_i^l \equiv X_i$, where in turn $i = 1, 2$. More generally, this condition is a characteristic of transitions continuous in extensive variables (here, quasi-second-order transitions) and, conveniently, allows the final theoretical relations for T_g to be written either in terms of mass fractions, M_i, or mole fractions. For the former, heat capacities are per unit mass, for the latter these are molar quantities. The choice of pure-component glass-transition temperatures as reference states provides the identity $S_i^{0,g} = S_i^{0,l}$. This and the composition continuity relations simplify eq 3 to

$$X_1\left\{\int_{T_{g_1}}^{T_g} (C_{p_1}^g - C_{p_1}^l)\,\mathrm{d}\ln T\right\} + X_2\left\{\int_{T_{g_2}}^{T_g} (C_{p_2}^g - C_{p_2}^l)\,\mathrm{d}\ln T\right\} + \Delta S_m^g - \Delta S_m^l = 0 \tag{4}$$

Derivation of an expression for mixed-system glass-transition temperatures from eq 4 turns primarily on considering the excess mixing entropy for the glassy and liquid states. The heat capacity increments occurring in eq 4 can be approximated to various degrees and present a secondary, later, question.

The class of mixtures for which ΔS_m and its behavior at T_g offer no problem are the ideal and regular solutions. In small-molecule mixtures ΔS_m would then be solely configurational and for segmentally mixed high molecular weight flexible polymers it would be conformational. In ideal and regular small-molecule mixtures ΔS_m is proportional to $X \ln X + (1 - X) \ln (1 - X)$, where X denotes X_1 or X_2; since the composition is fixed, the excess mixing entropy is continuous at T_g. For such polymer solutions an analogous continuity of ΔS_m arises at T_g. Generally, for ideal and regular solutions eq 4 reduces to[6,9]

$$X_1 \int_{T_{g_1}}^{T_g} \Delta C_{p_1}\,\mathrm{d}\ln T + X_2 \int_{T_{g_2}}^{T_g} \Delta C_{p_2}\,\mathrm{d}\ln T = 0 \tag{5}$$

where Δ denotes transition increments.

In compatible polymer mixtures, the presence of specific interactions and, for example, the dependence of ΔS_m on the intimacy of miscibility[11] render the excess mixing entropy problem more complex than that discussed above. Nevertheless, if mixing is relatively intimate, approaching the segmental level, the matter may be clarified sufficiently to yield a relation for the effect of composition on T_g in terms of pure-component properties.

It is of central importance to the theme of this discussion that the long-chain nature of high-polymer molecules (connectivity) has a profound effect on the excess entropy of mixing when the two components are miscible in a detailed sense, reducing ΔS_m to a value orders of magnitude below that if the mers were unconnected. Provided the severe connectivity constraint is maintained, factors such as the non-combinatorial "equation of state" contribution to ΔS_m,[12] specific interactions, non-random mixing, and so forth can be viewed as more or less moderate displacements of ΔS_m from a reference value (that of an ideal or regular solution). In the presence of secondary specific interactions, for which there is good evidence in at least one blend,[13,14] the connectivity property cannot but be maintained. Thus, to first order, the excess entropy of mixing for intimately mixed flexible high polymers can typically be considered negligible. Consequently, glass-transition temperatures in these blends are largely unaffected by ΔS_m and its behavior at T_g. This is particularly convenient as the influence of specific interactions, nonrandom mixing, and other effects render it unlikely that the excess mixing entropy is continuous at T_g. There is a quantitative argument concerning the relative magnitudes of the two contributions to the total system entropy which may be offered in support of this conclusion.

For ideal solutions of flexible high molecular weight polymers, ΔS_m is typically less than $\sim 2 \times 10^{-5}$ cal g^{-1} K^{-1} at ~ 300 K.[15,16] If factors altering the excess mixing entropy from an ideal solution value were collectively to increase the absolute value of this property by as much as an order of magnitude, then $\Delta S_m \sim 2 \times 10^{-4}$ cal g^{-1} K^{-1}. This, the maximum of ΔS_m, would occur at some intermediate system composition, when the absolute difference between T_g and the pure-component transition temperatures must also approach a maximum. At the appropriate M_i ($\sim 1/2$) deliberate choice of a relatively low value of this absolute difference (20 K) and typical values for the ΔC_{p_i} (~ 0.06 cal g^{-1} K^{-1}) gives the heat capacity terms of eq 4 as $\sim 2 \times 10^{-3}$ cal g^{-1} K^{-1}. For consistency T_g was taken as 300 K. This order of magnitude difference between the two terms would typically be maintained across the composition range. In the absence of primary interactions between molecules of the two components, the actual change in ΔS_m from an ideal solution value is unlikely to be as large as that given above. Further, a realistic maximum separation of T_g and the T_{g_i} could be considerably larger than 20 K.

The preceding qualitative and quantitative discussion provides a basis for the neglect of excess mixing entropies for at least one class of compatible polymer pairs. For these blends, eq 5 may be used to describe the compositional variation of T_g. The formal equivalence thus established between the effect of composition on glass-transition temperatures in ideal and regular solutions and compatible polymer blends arises, though, from the connectivity property of high polymers and cannot be taken as evidence of any further connections between these mixtures.

In view of the first-order nature of this theory it would seem inconsistent to derive explicit relations for the composition dependence of T_g other than in first approximation. Therefore, theoretical relations for the effect are given here on the basis of temperature-independent heat-capacity increments. Comparison between theory and experiment makes use of expressions so derived, the most general of which is

$$X_1 \Delta C_{p_1} \ln (T_g/T_{g_1}) + X_2 \Delta C_{p_2} \ln (T_g/T_{g_2}) = 0 \quad (6)$$

For later convenience the X_i are exchanged for mass fractions (recall that the ΔC_{p_i} are then per unit mass) and eq 6 becomes

$$\ln T_g = \frac{M_1 \Delta C_{p_1} \ln T_{g_1} + M_2 \Delta C_{p_2} \ln T_{g_2}}{M_1 \Delta C_{p_1} + M_2 \Delta C_{p_2}} \quad (7)$$

or, equivalently,

$$\ln (T_g/T_{g_1}) = \frac{M_2 \Delta C_{p_2} \ln (T_{g_2}/T_{g_1})}{M_1 \Delta C_{p_1} + M_2 \Delta C_{p_2}} \quad (8)$$

Four particular nontrivial cases of the general mixing relation arise, as is discussed below.

If the ratio T_{g_1}/T_{g_2} is not greatly different fron unity, the logarithmic terms of eq 8 may be approximated in the usual manner to give

$$T_g \simeq \frac{M_1 \Delta C_{p_1} T_{g_1} + M_2 \Delta C_{p_2} T_{g_2}}{M_1 \Delta C_{p_1} + M_2 \Delta C_{p_2}} \quad (9)$$

which is formally identical to the Wood equation[17] (originally derived for random copolymers), but unlike the latter contains no adjustable parameters. Other familar expressions can be derived from eq 8 and 9. For example, the empirical rule $\Delta C_{p_i} T_{g_i} \simeq$ constant[18] when substituted in eq 9 gives the familiar Fox equation[2]

$$\frac{1}{T_g} \simeq \frac{M_1}{T_{g_1}} + \frac{M_2}{T_{g_2}} \quad (10)$$

and is consistent with the observation that if T_{g_2} is chosen as the higher pure-component transition temperature, T_g is typically a convex function of M_2.

This work presented here also provides a thermodynamic basis for the recent observation by Pochan, Beatty, and Hinman[19] that data on the composition dependence of T_g for a number of polymer systems can be reproduced approximately by the equation

$$\ln T_g = M_1 \ln T_{g_1} + M_2 \ln T_{g_2} \quad (11)$$

In the context of this theory eq 11 follows from eq 7 if $\Delta C_{p_1} = \Delta C_{p_2}$. Thus, the correlation observed by Pochan et al. is not necessarily of kinetic[19] origin. A fourth version of eq 7 is obtained if both pure-component heat capacity increments have the same value and the logarithmic functions are suitably expanded. This expression

$$T_g \approx M_1 T_{g_1} + M_2 T_{g_2} \quad (12)$$

therefore can also be obtained from eq 11.

As both total entropy and total volume are continuous at glass-transition temperatures there are two, complementary, bases for the derivation of mixing relations. Consequently, the derivation of a relation for T_g in terms of pure-component properties from the mixed-system volume is outlined below. The volume analogue of eq 1 is defined in terms of mole fractions, pure-component molar volumes, V_i, and the molar excess mixing volume, ΔV_m; molar volumes referred to the T_{g_i} are denoted by V_i^0, and isobaric volume thermal expansivities $\alpha_i \equiv (1/V_i^0) \cdot (\partial V_i/\partial T)_p$ are introduced, leading to (cf. eq 4)

$$X_1 V_1^0 \Delta\alpha_1 (T_g - T_{g_1}) + X_2 V_2^0 \Delta\alpha_2 (T_g - T_{g_2}) + \Delta V_m^l - \Delta V_m^g = 0 \quad (13)$$

where Δ again denotes transition (glass to liquid) increments. In terms of pure-component volume fractions, $\phi_i^0 \equiv X_i V_i^0/(X_1 V_1^0 + X_2 V_2^0)$, and the excess volume fractions, $\phi_m^g \equiv \Delta V_m^g/(X_1 V_1^0 + X_2 V_2^0)$, $\phi_m^l \equiv \Delta V_m^l/(X_1 V_1^0 + X_2 V_2^0)$, eq 13 may be written as

$$\phi_1^0 \Delta\alpha_1 (T_g - T_{g_1}) + \phi_2^0 \Delta\alpha_2 (T_g - T_{g_2}) + \phi_m^l - \phi_m^g = 0 \quad (14)$$

For mixtures in which either $\Delta V_m^g \equiv \Delta V_m^l$ or the excess mixing volumes are finite but negligible compared to $\phi_i^0 \Delta\alpha_i (T_g - T_{g_i})$, glass-transition temperatures are given by

$$T_g \approx \frac{\phi_1^0 \Delta\alpha_1 T_{g_1} + \phi_2^0 \Delta\alpha_2 T_{g_2}}{\phi_1^0 \Delta\alpha_1 + \phi_2^0 \Delta\alpha_2} \quad (15)$$

This equation is formally identical to an expression obtained from the linear additivity of pure-component free volumes, though the definitions of the α_i and ϕ_i^0 differ somewhat.[8,9]

Ideal mixtures are necessarily described by eq 15. Its suitability for mixtures with nonzero excess mixing volumes is, however, a matter for enquiry. The relative magnitudes of the two types of terms in eq 14 may be estimated readily. A typical value for the $\Delta\alpha_i$ is taken to be $\sim 5 \times 10^{-4}$ K^{-1}. If, as before, $T_g - T_{g_i} \sim 20$ K and $\phi_i^0 \sim {}^1/_2$, the terms in $\Delta\alpha_i$ are $\sim 5 \times 10^{-3}$. Taking as a rough guide to the validity of eq 15 the condition that $\phi_i^0 \Delta\alpha_i (T_g - T_{g_i})$ estimated from values given above should exceed the absolute value of $\phi_m^1 - \phi_m^g$ by an order of magnitude, the latter term must not exceed 5×10^{-4} (0.05%) at T_g. It is important to note that connectivity should not affect ΔV_m to the extent it influences ΔS_m and, further, that (negative) volumes of mixing reported for several blends[16,20] (though not at T_g) typically exceed ~1%. Moreover, the free-volume expression formally identical to eq 15 does not predict T_g correctly when specific interactions are present.[16] This seems to suggest that eq 8 might be of somewhat more general use than eq 15, although a more definite statement must await careful experimentation and further theoretical enquiry.

Formal considerations have thus far been limited to blends at constant pressure. Conveniently, the derived mixing relations can be readily adapted to include the effect of pressure. Subject to the reasonable neglect of terms in $\mathrm{d}\Delta C_{p_i}/\mathrm{d}p$ as second-order effects, eq 7 and 9 yield, respectively, the expressions

$$\frac{\mathrm{d} \ln T_g}{\mathrm{d}p} \simeq \frac{M_1 \Delta C_{p_1} \dfrac{\mathrm{d} \ln T_{g_1}}{\mathrm{d}p} + M_2 \Delta C_{p_2} \dfrac{\mathrm{d} \ln T_{g_2}}{\mathrm{d}p}}{M_1 \Delta C_{p_1} + M_2 \Delta C_{p_2}} \tag{16}$$

and

$$\frac{\mathrm{d}T_g}{\mathrm{d}p} \simeq \frac{M_1 \Delta C_{p_1} \dfrac{\mathrm{d}T_{g_1}}{\mathrm{d}p} + M_2 \Delta C_{p_2} \dfrac{\mathrm{d}T_{g_2}}{\mathrm{d}p}}{M_1 \Delta C_{p_1} + M_2 \Delta C_{p_2}} \tag{17}$$

Four other predictive relations for the pressure dependence of T_g can be derived, one from each of eq 10–12 and 15.

Comparison of Predicted and Observed Composition Dependence of T_g

A critical test of the theoretical relations requires, generally, that the principal and subsidiary conditions necessary for their derivation be met. The blends considered should of course be largely, if not entirely, amorphous, in order to obviate the possible influence of crystallinity. Further, those relations derived from the entropy require that miscibility approach the segmental level. If a principal condition is departed from significantly, comparison of observed and predicted values of T_g may be advantageous, though of supplementary usefulness.

The poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and polystyrene (PS) system is probably the most studied compatible polymer blend. It has been judged compatible by a variety of methods,[21] exhibiting a single composition dependent T_g for all relative proportions according to differential scanning calorimetry (DSC),[16,22,23] thermomechanical,[24] dynamic mechanical,[23,25] thermal optical analysis,[22,26] and dielectric methods.[11] Additionally, there is direct calorimetric evidence for the expected negative heat of mixing, ΔH_m, across the range of composition,[27] a sufficient but not necessary criterion for compatibility (the mixing is sufficiently intimate that ΔS_m is considered negligible[27]). This negative value of ΔH_m is consistent with evidence for phenyl-group coupling[14] and, certainly, the formation of these secondary bonds must be considered suggestive of interaction at a somewhat detailed level, and possibly intimate mixing. Also, DSC thermograms for these blends show less than the considerable thermal broadening vis-à-vis pure components observed for a related compatible polymer pair.[16,28] The existence of local concentration variations for the PPO/PS blend cannot, though, be excluded. This blend therefore seems suitable for application of those theoretical relations derived from the entropy continuity condition; there are definite indications of rather intimate mixing, and the PPO/PS interaction is secondary (the presence of substantial interactions between the two components is a topic for later discussion). Turning now to the validity of a relation such as eq 15, based on the neglect of ΔV_m, it should be noted that this quantity has been observed as significant for the PPO/PS blend.[16]

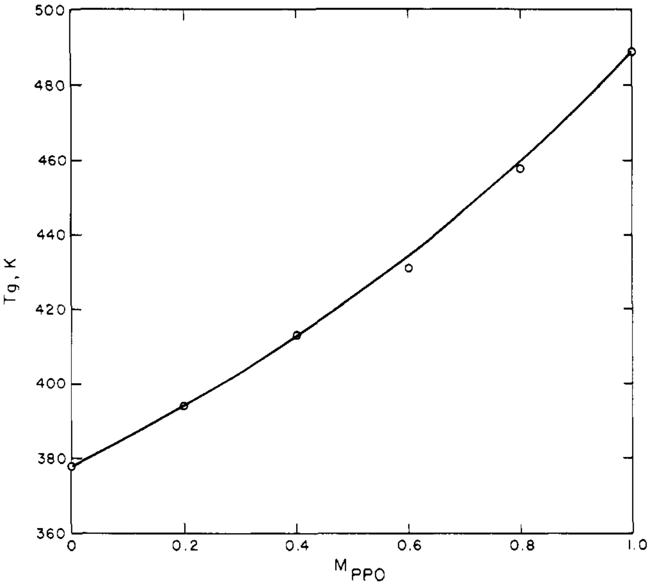

Figure 1. Glass-transition temperatures, T_g, of PPO/PS blends vs. mass fraction of PPO, M_{PPO}. The full curve was calculated from eq 8. Fried's experimental values of T_g[16] are represented as circles. Data[16] for eq 8: $\Delta C_{p_1} = 0.0671$ cal K^{-1} g^{-1}, $\Delta C_{p_2} = 0.0528$ cal K^{-1} g^{-1}; $T_{g_1} = 378$ K, $T_{g_2} = 489$ K. PPO was designated as component 2. All calculated temperatures were rounded to the nearest degree.

In order to compare theory and experiment in a self-consistent manner, it is necessary to seek blend data determined in the same manner as for the pure-component transition heat capacity increments and glass-transition temperatures. This is to ensure that any significant differences between predicted and observed values of T_g can be ascribed to genuine discrepancies and, similarly, agreement can be taken as genuine. Fried[16] has recently studied several properties of two largely amorphous polymer blends, PPO/PS and PPO/poly(styrene-*co*-4-styrene). The pure component and blend glass transitions were determined in a Perkin-Elmer DSC II at a heating rate of 20 K min^{-1}. The PPO was additive free; details of sample preparation and other relevant experimental data are given elsewhere.[16] The glass-transition temperature was in all cases taken at the midpoint of the transition heat capacity increment. The associated uncertainty in T_g was estimated as 2 K.

Theoretical values for the compositional variation of T_g for PPO/PS blends were calculated from eq 8 and, as Figure 1 demonstrates, these agree well with Fried's experimental results. The accuracy of various approximations to eq 8 has also been considered. Table I lists predicted values of T_g from, in order, eq 8–12. As expected, the predictions of eq 8 are closest to the experimental values. For the PPO/PS blend, eq 9 also predicts values

Table I
Comparison of Predicted and Observed Values of T_g for Various Compositions of PPO/PS Blends

mass fraction of PPO (M_{PPO})	glass transition temp, T_g, in K					
	exptl[16]	eq 8	eq 9	eq 10	eq 11	eq 12
0	378	378	378	378	378	378
0.2	394	394	396	396	398	400
0.4	413	413	416	416	419	422
0.6	431	434	438	438	441	445
0.8	458	460	462	462	465	467
1.0	489	489	489	489	489	489

of T_g close to the observed results. Further, since the product $\Delta C_{p_i} T_{g_i}$ for the two components is respectively 25.8 cal g^{-1} (PPO) and 25.4 cal g^{-1} (PS), the predictions of eq 9 and 10 differ little. Both of these expressions are somewhat more accurate than the logarithmic rule of mixtures applied to glass-transition temperatures. Clearly, however, the combination of circumstances necessary for these results will not invariably arise.

Turning to the mixing relation derived from the volume continuity condition, Fried[16] has considered the reported $\Delta\alpha_i$ and shown that T_g is predicted to be a concave function of the variable M_{PPO}, whereas Figure 1 illustrates that T_g is actually a convex function of M_{PPO}. Thus the observed and predicted compositional variation of T_g disagree even qualitatively. This fundamental difference is consistent with earlier comments on the possible inadequacy of eq 15.

Since the PPO/PS compatible pair seems appropriate for realistic application of the theory and good agreement is found with experiment, the theory might be applied usefully to other compatible polymer mixtures and to the parallel phenomenon when two pure components are made into a random copolymer. For blend systems other than PPO/PS there is relatively less information concerning the type and level of compatibility. For example, DSC evidence is generally available, allied perhaps with the results of dielectric measurements and the rough guide of optical clarity. To seek limits of the theory a blend derived from the PPO/PS system but known to be less compatible is considered next.

Random copolymers of styrene (S) and *p*-chlorostyrene (pClS) blended with PPO have been found compatible by DSC, thermal optical analysis, dielectric, dynamic mechanical, and density measurement.[16,25] For copolymers containing ≲67.1 mol% of pClS, compatibility occurs for all relative proportions of the pure components. DSC thermograms show considerable transition broadening compared with the parent copolymer and PPO components.[16] Dielectric studies demonstrate a parallel relative broadening of the relaxation spectra in the compatible blend, which can be interpreted as arising from a range of local concentrations.[28] A second peak generally observed in phase-separated mixtures is not seen in the region of compatibility. Further, the compatibility/incompatibility transition is rather clear on the DSC thermograms. Outside the region of compatibility two largely constant glass transitions characteristic of the pure components are observed.[16] In summary, there would seem to be distinct miscibility, but it is somewhat unlikely that this extends to the segmental level.

The compositional variation of T_g for a PPO/S-pClS copolymer blend has been calculated from eq 8 for the copolymer with 58.5 mol % *p*-chlorostyrene. The predicted and observed relations between blend glass-transition temperatures and mass fraction of PPO are depicted in Figure 2. Equation 8 predicts the observed behavior very well.[29] Thus, although the transitions at intermediate compositions are rather broad, the theory is quite acceptable for a composition which approximates the macroscopic mass proportions.

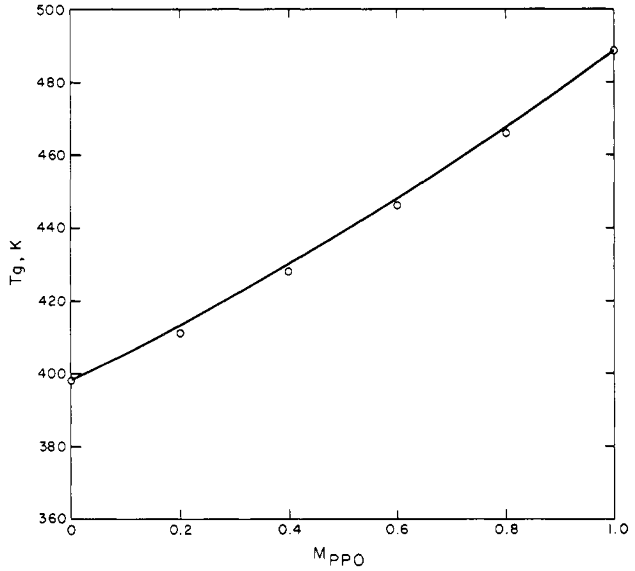

Figure 2. Glass-transition temperatures of PPO/poly(styrene-*co*-*p*-chlorostyrene) blends vs. mass fraction of PPO. The full curve was calculated from eq 8. The circles represent data taken from Fried.[16] For the copolymer,[16] ΔC_{p_1} = 0.0593 cal K^{-1} g^{-1}, T_{g_1} = 398 K. Data for PPO as for Figure 1.

Concluding Remarks

It has been demonstrated that an elementary relation for the effect of composition on glass-transition temperatures in compatible polymer mixtures, based on the mixed system entropy continuity at T_g, serves to describe the phenomenon from pure-component properties. This relation arises in part from a special property of polymer molecules (specifically, their long chain nature (connectivity)) which reduces the excess mixing entropy to a typically negligible value. The final theoretical relations predict the observed effect of composition on glass-transition temperatures surprisingly well for two polymer blends, a result which may be considered to reflect successfully on the neglect of excess mixing entropy. Further, the central predictive relation serves to unify the basis for the form of four equations for the phenomenon and can be extended to predict the pressure dependence of T_g for polymer blends. In view of the success of such a simple treatment the theory might be usefully extended.

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(29) The theoretical predictions for the other compatible PPO/copolymer blend (67.1 mol % pClS) investigated by Fried[16] are very close to those for the blend of Figure 2, as are the experimental results.

Thermodynamic Perturbation Theory of Phase Separation in Macromolecular Multicomponent Systems. 2. Concentration Dependence[†,‡]

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ABSTRACT: A perturbation-theoretical approach to the concentration dependence of phase separation in quasiternary macromolecular solutions consisting of polymer, solvent, and nonsolvent is developed. It results in a linear semilogarithmic phase equation $\gamma_F^* = A_c - \sigma_c^* \ln c_0$, where γ_F^* denotes the precipitant fraction (volume fraction of the precipitant at the cloud point) and c_0 the initial polymer concentration in g/cm^3. Here, A_c and σ_c^* are constants with A_c as the precipitant fraction at $c_0 = 1$ g/cm^3 and σ_c^* the inverse value of the change of the relative perturbation density ($\Delta\mu^*_{\mathcal{P}F,c}$). The theory is verified experimentally at 25 °C by investigation of the three different systems: (a) polystyrene–benzene–methanol; (b) poly(methyl methacrylate)–benzene–cyclohexane; (c) poly(ϵ-caprolactam)–*m*-cresol–petroleum ether. Fast turbidimetric titration measurements on the basis of the dynamic volume pulse technique were used. The perturbation-theoretical approach is confirmed furthermore by numerous experimental results taken from the literature. The results are compared critically with the earlier approaches on the basis of statistical thermodynamics, partition equilibria, and solution equilibria. In this context, the effect of the constant ratio of the solvent/nonsolvent in the gel phase is interpreted theoretically.

I. Introduction

This paper is concerned with a perturbation-theoretical approach to the initial concentration dependence of phase separation in macromolecular multicomponent systems after the addition of nonsolvent (precipitant), and with applications of the theory. The approach is based on concepts that I have developed in previous papers.[1-3] The assumptions and basic equations have been set out in the first paper of this series.[3]

Firstly, it is shown how the perturbation relations can be applied to calculating the functional dependence of the precipitant fraction (volume fraction of the nonsolvent at the precipitation threshold, γ_F^*) from the original polymer concentration, taking into account the macromolecular phase concentrations. Then, the theory is applied to various multicomponent macromolecular systems. The results obtained are scrutinized and compared critically with earlier attempts at problem solution such as, e.g., partition equilibria[4,5] and solution equilibria.[6,7]

II. Fundamentals: The Perturbation-Theoretical Approach of Phase Separation in Fluid Macromolecular Multicomponent Systems

Addition of nonsolvent to a homogeneous macromolecular solution may cause its disintegration by polymer precipitation. The simplest system here is now a fluid heterogeneous ternary one. Generally, however, solutions of macromolecules in solvent/nonsolvent mixtures are quasiternary multicomponent systems. In the following, the assumptions and the notation of ref 3 are used.

Let the finite set of a multicomponent macromolecular solution of nonelectrolytes $|K_0 = \{1, 2, ..., L_\lambda, ..., \mathcal{P}_j, ..., F_{\varkappa-1}, F_{\varkappa+1}, ..., r\}$ be perturbed by the admixture of a nonsolvent $F_\varkappa \notin |K_0$. Then, the system passes from the reference state $|K_0 \rightarrow |K = \{1, 2, ..., L_\lambda, ..., \mathcal{P}_j, ..., F_\varkappa, ..., r\} = |K_0 + \{F_\varkappa\}$, $F_\varkappa \in |K \supset |K_0((j,\lambda,\varkappa) \in N_{r(j,\lambda,\varkappa)})$. Let the statistical polymer component in the precipitation equilibrium which is

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[†] This paper is dedicated to Professor Maurice L. Huggins on the occasion of his 80th birthday, but publication unfortunately had to be delayed.

[‡] Presented at the 76th Annual General Meeting of the Deutsche Bunsen-Gesellschaft für Physikalische Chemie in Braunschweig, May 19–21, 1977.

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