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Thermodynamics and the Compositional Variation of Glass Transition Temperatures

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ABSTRACT: Excess properties of mixing of the thermodynamic theory for the compositional variation of glass transition temperatures are shown to be determined uniquely by the internal consistency of the general solution relations used in the theory. For the glassy state these excess properties involve solution properties and pure constituent properties of this state alone. Excess properties for the liquid state are likewise phase-consistent. From the entropy, volume, and enthalpy, general and equivalent tautological relations are derived for the compositional variation of glass transition temperatures. These reduce to separate and specific relations of approximate predictive use for in turn random, volume-additive, and athermal solutions. The formal consequences of the simultaneous validity of two or more of these different predictive theories demonstrate that such overlap would not be at all general.

Introduction

A classical thermodynamic approach I have used to provide a theory for the compositional variation of glass transition temperatures[1–9] has been said by Goldstein[10] to be incorrect. In particular, he contends that for the excess entropy of mixing of the glass the pure-constituent entropies should not all be of the glass but should be of the actual states at the conditions of interest. On the basis of this contention he claims that the predictive entropic relations I have used do not have a basis in thermodynamics per se. Their origin and success are attributed instead to the Gibbs–DiMarzio molecular theory of the glass transition,[11] a quasi-macroscopic version of which[12] can give relations identical in form with those I have used.

That an entropic relation of the thermodynamic approach does not always give exact agreement with the data is offered as support for the view that this approach is not correct. Also, the predictive entropic, volume-based, and enthalpic theories, which are particular versions of the corresponding tautologies, are compared as if these were equivalent general descriptions and as if the conditions of their consistency were an essential consequence of the thermodynamic approach. Problems are also imputed to the tautologies themselves. For example, the transition behavior of the excess volumes of mixing required by the corresponding tautology is said to be implausible.

These various claims, assertions, and interpretations are taken up below in a summary of the elements of the derivation of general thermodynamic relations for the compositional variation of glass transition temperatures and the restrictions necessary for these to be of predictive use.

The Model of the Glass Transition

Here, as previously,[1–9] the glass transition is treated formally as if it were equivalent to an Ehrenfest transition of second order.[13] In this context the only feature specific to the glass transition in the discussion below is notational. In this discussion properties of the liquid and glass are denoted by the superscripts l and g, respectively.

The aim of the thermodynamic theory to be outlined is the provision of relations between the glass transition temperature, T_g, of a single-phase solution of fixed but arbitrary composition and the glass transition temperatures, T_{g_i}, of the pure constituents from which the solution is formed. In the thermodynamic model the solution entropy, volume, and enthalpy, in turn S, V, and H, are continuous at T_g and various first derivatives of these undergo characteristic and finite discontinuities.[13] Similarly, at the T_{g_i} the variables S_i, V_i, and H_i of the separate pure constituents are continuous and various first derivatives of these undergo characteristic transition discontinuities. It is these general features of second-order transitions that are used in conjunction with the general solution relations to derive thermodynamic relations for the compositional variation of T_g.

Derivation of the Tautologies and Their Predictive Versions

The Entropic Relations. Because the nature of the excess entropies of mixing of the solution relations used in the theory is an essential point, the entropic theory is considered first. For each of the two states of the glass transition a formal connection is defined between the solution entropy and the phase-identical pure constituent properties in the same amounts, X_i, that these are present in the solution. In these solution relations[1,10]

$$S^l = \sum X_i S_i^{\,l} + \Delta S_{\text{mix}}^{\,l} \qquad \text{(1a)}$$

and

$$S^g \equiv \sum X_i S_i^{\,g} + \Delta S_{\text{mix}}^{\,g} \qquad \text{(1b)}$$

the terms $\Delta S_{\text{mix}}^{\,l}$ and $\Delta S_{\text{mix}}^{\,g}$ are the excess entropies of mixing of the liquid and glass, respectively. The sum in eq 1 and in all other relations of this paper are over all of the constituents of the solution.

The solution relations of eq 1 are formal devices through which solution and pure constituent properties of the same phase are connected. In each of these relations both the solution entropy and the pure constituent sum are specified; the single remaining term in each of these linear relations is thereby completely determined and cannot be fixed independently. Explicitly, from eq 1a the excess entropy of mixing of the liquid is the unique solution of this relation in terms of the quantities specified,

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$$\Delta S_{\mathrm{mix}}^{1} = S^{1} - \sum X_i S_i^{1} \tag{2a}$$

and from eq 1b the excess entropy of mixing of the glass is the unique solution of this relation in terms of the solution entropy and the pure constituent sum,

$$\Delta S_{\mathrm{mix}}^{\mathrm{g}} = S^{\mathrm{g}} - \sum X_i S_i^{\mathrm{g}} \tag{2b}$$

Equally, eq 2a and 2b are the explicit consequences of the absolute requirement that eq 1a and 1b are each self-consistent.

Thus, the excess entropies of mixing are fixed entirely by the properties prescribed in the solution relations and are the phase-consistent quantities of eq 2. For the glass the excess entropy of mixing is the difference between properties of the glass alone, just as the excess entropy of mixing of the liquid involves properties of this state alone. A corollary of this result is that the use in eq 1 of other than the phase-consistent excess properties of eq 2 is never correct. In particular, Goldstein's claim[10] that the excess entropy of mixing of the glass in eq 1b involves the entropies of the pure constituents "...in whichever state, liquid or glass, that is the usual state..." at the conditions of interest is incorrect as this would violate the internal consistency of the solution relations.[14]

The solution relations of eq 1 are used as follows in the derivation of a general relation between the solution glass transition temperature and the T_{g_i}. At fixed pressure the solution glass-transition occurs at temperatures T_{g} such that

$$S^{1}(T_{\mathrm{g}}) = S^{\mathrm{g}}(T_{\mathrm{g}}) \tag{3}$$

From eq 1, this can be rewritten identically as

$$\sum X_i S_i^{1} + \Delta S_{\mathrm{mix}}^{1} = \sum X_i S_i^{\mathrm{g}} + \Delta S_{\mathrm{mix}}^{\mathrm{g}} \tag{4}$$

The pure constituent entropies in eq 4 are referred to their corresponding T_{g_i} through the use of the isobaric heat capacities C_{p_i}.[1,13] Explicitly, for the liquid and glassy states respectively

$$S_i^{1}(T_{\mathrm{g}}) = S_i^{1}(T_{\mathrm{g}_i}) + \int_{T_{\mathrm{g}_i}}^{T_{\mathrm{g}}} (C_{p_i}^{1}/T)\,\mathrm{d}T \tag{5a}$$

and

$$S_i^{\mathrm{g}}(T_{\mathrm{g}}) = S_i^{\mathrm{g}}(T_{\mathrm{g}_i}) + \int_{T_{\mathrm{g}_i}}^{T_{\mathrm{g}}} (C_{p_i}^{\mathrm{g}}/T)\,\mathrm{d}T \tag{5b}$$

From eq 5, the pure constituent conditions

$$S_i^{1}(T_{\mathrm{g}_i}) = S_i^{\mathrm{g}}(T_{\mathrm{g}_i}) \tag{6}$$

and the definitions

$$C_{p_i}^{1} - C_{p_i}^{\mathrm{g}} = \Delta C_{p_i} \tag{7}$$

eq 4 can be written as

$$\sum X_i \int_{T_{\mathrm{g}_i}}^{T_{\mathrm{g}}} (\Delta C_{p_i}/T)\,\mathrm{d}T + \Delta S_{\mathrm{mix}}^{1} - \Delta S_{\mathrm{mix}}^{\mathrm{g}} = 0 \tag{8}$$

In the thermodynamic model eq 8 is equivalent to eq 4, which in turn is identical with eq 3, the defining condition for the solution transition. The excess entropies of mixing of eq 8 are the phase-consistent quantities of eq 2, carried through from the solution relations of eq 1. While it is general for single-phase solutions, eq 8 is, however, a formal tautology because the solution relations used to derive it are tautologies.

This establishes that the excess properties of mixing in the entropic tautology for the compositional variation of T_{g}, from which the predictive theory I have used is obtained, are indeed phase-consistent quantities. There are two parts of the derivation of a predictive version of eq 8. First, the formal supposition that for random solutions the difference between the excess entropies of mixing is dominated by the difference between the combinatorial contributions to these quantities. Second, the familiar approximation that these combinatorial contributions can be written completely and explicitly as a function of the compostion alone. An example of such a function is the Flory–Huggins expression,[15] although for the present purpose the actual function is not needed. For random mixing problems in some generality, then (including the particular case of miscible blends of high polymers, for which[15] $\Delta S_{\mathrm{mix}} \simeq 0$) the tautology of eq 8 becomes the approximate predictive relation

$$\sum X_i \int_{T_{\mathrm{g}_i}}^{T_{\mathrm{g}}} (\Delta C_{p_i}/T)\,\mathrm{d}T = 0 \tag{9}$$

As outlined above, the basis of eq 9 lies in classical thermodynamics and in the nature of approximate relations for excess entropies of mixing derivable from statistical thermodynamics. Consequently, the predictive theory for the compositional variation of T_{g} embodied by eq 9 has a basis in thermodynamics alone, independent of any molecular theory or interpretation of the glass transition.

As discussed later, the entropic theory for the compositional variation of glass transition temperatures has been taken to be quite widely applicable to solutions on the premise that many of these might reasonably be expected to be largely random. For problems not of solutions per se (for example, the effect of copolymerization on T_{g}[6]) it has been used on the premise that these can be modeled in terms of equivalent random solutions.

Comparison of predicted and observed values of T_{g} is through the use of integrated forms of eq 9. This requires specific assumptions about the temperature dependence of the ΔC_{p_i}, a dependence which is not generally known. Consequently, integrated versions of eq 9 are inexact relations. The expression derived in the (zeroth order) approximation that the ΔC_{p_i} are uniformly independent of temperature,

$$\ln T_{\mathrm{g}} = \frac{\sum X_i \Delta C_{p_i} \ln T_{\mathrm{g}_i}}{\sum X_i \Delta C_{p_i}} \tag{10}$$

has met with success.[1-9] For certain plasticized polymers, when the T_{g_i} are rather far apart, the temperature dependence of the ΔC_{p_i} must be incorporated in eq 9 to give reasonable agreement between calculated and observed values of T_{g}.[16,17] The assumption that the ΔC_{p_i} are inversely proportional to temperature is convenient here as it is consistent with the tendency of these to diminish as a function of increasing temperature[18] and leads to a relation free of adjustable parameters,

$$T_{\mathrm{g}} = \frac{\sum X_i \Delta C_{p_i} T_{\mathrm{g}_i}}{\sum X_i \Delta C_{p_i}} \tag{11}$$[19]

In eq 11 the ΔC_{p_i} are at their corresponding T_{g_i} and thus can be determined directly. Here it is useful to emphasize that notwithstanding the success of eq 10 and 11 the two associated relations between the ΔC_{p_i} and temperature are simply convenient methods for the estimation of the integrals of eq 9. Neither dependence has a compelling general basis and there may well be problems for which neither of these two methods is acceptable.

The entropic theory, in the form of eq 9 and integrated verions thereof, is a compromise between the disparate aims of predictive simplicity and a fair measure of a priori applicability. Even for solutions that are largely random, eq 9 is not exact. Therefore, the use of the theory is an approximate exercise with an innate heuristic element. In circumstances of this kind it is to be expected that the theory will not always give exact agreement with the data.[20] To imply, as Goldstein does, that the approach is flawed in an essential way if eq 10 does not give exact agreement with the data for all systems is wrong. Exact agreement between theory and experiment is required only of thermodynamic relations that are general, rigorous, and exact or, for specific theories, when all assumptions are met exactly.

The Volume-Based Relations. Again, for each of the two states of the glass transition a relation is prescribed between the solution quantity and the phase-identical pure constituent quantities. These relations, the volume analogues of eq 1, are

$$V^{l} \equiv \sum X_i V_i^{l} + \Delta V_{\mathrm{mix}}{}^{l} \tag{12a}$$

and

$$V^{g} \equiv \sum X_i V_i^{g} + \Delta V_{\mathrm{mix}}{}^{g} \tag{12b}$$

Equations 12 determine the excess volumes of mixing uniquely in terms of the properties specified as

$$\Delta V_{\mathrm{mix}}{}^{l} = V^{l} - \sum X_i V_i^{l} \tag{13a}$$

and

$$\Delta V_{\mathrm{mix}}{}^{g} = V^{g} - \sum X_i V_i^{g} \tag{13b}$$

That is, for eq 12 to be self-consistent the excess volumes of mixing for the liquid and the glass are both phase-consistent quantities given uniquely by eq 13. This means that the volume solution relations, eq 12, are tautologies, as are the entropic solution relations, eq 1.

In terms of the volume, the defining conditions of the isobaric glass transition for the solution is that this occurs at temperatures T_g such that

$$V^{l}(T_g) = V^{g}(T_g) \tag{14}$$

This condition can be rewritten from eq 12 as, identically,

$$\sum X_i(V_i^{l} - V_i^{g}) + \Delta V_{\mathrm{mix}}{}^{l} - \Delta V_{\mathrm{mix}}{}^{g} = 0 \tag{15}$$

To introduce the T_{g_i}, these are used as reference temperatures for the pure constituent volumes in eq 15 in conjunction with pure constituent volume expansivities, α_i.[13] This use, the conditions

$$V_i^{l}(T_{g_i}) = V_i^{g}(T_{g_i}) \tag{16}$$

and the definitions

$$(V_i\alpha_i)^{l} - (V_i\alpha_i)^{g} = \Delta(V_i\alpha_i) \tag{17}$$

give that at T_g the pure constituent differences of eq 15 are

$$V_i^{l} - V_i^{g} = \int_{T_{gi}}^{T_g} \Delta(V_i\alpha_i)\,\mathrm{d}T \tag{18}$$

From eq 18, eq 15 can be rewritten as

$$\sum X_i \int_{T_{gi}}^{T_g} \Delta(V_i\alpha_i)\,\mathrm{d}T + \Delta V_{\mathrm{mix}}{}^{l} - \Delta V_{\mathrm{mix}}{}^{g} = 0 \tag{19}$$

In the thermodynamic model of the glass transition this formal tautology is equivalent to the defining condition for the solution transition, eq 14. The excess volumes of mixing of eq 19 are the phase-consistent quantities of eq 13.

From eq 19, any discontinuity that might occur in ΔV_{mix} at T_g is balanced exactly by a discontinuity in the pure constituent sum of this relation. This is a consequence of eq 19 pointed out by Goldstein[10] and one to which he objects, through an appeal to sentiment.[21] To illustrate directly the origin of this exact compensation, from eq 12 in the form of eq 13, generally

$$\Delta V_{\mathrm{mix}}{}^{l} - \Delta V_{\mathrm{mix}}{}^{g} = (V^{l} - V^{g}) - \sum X_i(V_i^{l} - V_i^{g}) \tag{20}$$

From eq 14, at T_g this reduces to

$$\Delta V_{\mathrm{mix}}{}^{l} - \Delta V_{\mathrm{mix}}{}^{g} = -\sum X_i(V_i^{l} - V_i^{g}) \tag{21}$$

which is identical with eq 15. As eq 20 and 21 demonstrate, the exact compensation is the condition of the continuity of the solution volume at T_g as expressed through the solution relations. Equation 19 is merely a further and useful particularization of this condition, through the use of eq 18. In view of the straightforward, in one sense, trivial nature of the compensation as a restatement of a tautology, eq 19 offers no difficulty in interpretation.

Were the excess properties of mixing of the entropic and enthalpic analogues of eq 19 to be discontinuous at the solution glass transition, an exact compensation precisely analogous to that for the volume relation must occur. Again, this is no more than a reflection of the continuity of the corresponding solution quantity at T_g.

To consider the circumstances for which the volume-based tautology would reduce to a predictive relation, first it should be noted that it is generally to be expected that solutions have nonzero excess volumes of mixing. Pertinent to this, solution theory provides no expression for ΔV_{mix} in say composition alone (analogous to that for ΔS_{mix}) to indicate that in any generality this may be continuous at a second-order transition. The absence of any evident basis for supposing that eq 19 usually reduces to a predictive relation is taken to indicate that it does not. This tautology, though, necessarily becomes predictive when the excess volumes of mixing for the liquid and glass both vanish or are negligible. Thus, only for solutions for which eq 19 it is at least approximately true that

$$\Delta V_{\mathrm{mix}}{}^{l} = 0 = \Delta V_{\mathrm{mix}}{}^{g} \tag{22}$$

does the relation

$$\sum X_i \int_{T_{gi}}^{T_g} \Delta(V_i\alpha_i)\,\mathrm{d}T = 0 \tag{23}$$

arise and are predictive volume-based relations for T_g obtained. The simplest integrated form of eq 23 for such volume-additive solutions arises if the $\Delta(V_i\alpha_i)$ are taken as temperature-independent. The solution glass transition temperature is then approximately

$$T_g = \frac{\sum X_i \Delta(V_i\alpha_i) T_{g_i}}{\sum X_i \Delta(V_i\alpha_i)} \tag{24}$$

The Enthalpic Relations. For the liquid and glass respectively

$$H^{l} \equiv \sum X_i H_i^{l} + \Delta H_{\mathrm{mix}}{}^{l} \tag{25a}$$

and

$$H^{g} \equiv \sum X_i H_i^{g} + \Delta H_{\mathrm{mix}}{}^{g} \tag{25b}$$

From eq 25, the excess enthalpies of mixing are uniquely

$$\Delta H_{\mathrm{mix}}{}^{l} = H^{l} - \sum X_i H_i^{l} \tag{26a}$$

and

$$\Delta H_{\mathrm{mix}}{}^{g} = H^{g} - \sum X_i H_i^{g} \tag{26b}$$

Thus, as for all excess properties of mixing of theories using phase-identical solution relations of the form of eq 1, the excess enthalpies of mixing are phase-consistent quantities.

The isobaric glass transition occurs at temperatures T_g such that

$$H^{l}(T_g) = H^{g}(T_g) \qquad (27)$$

which, from eq 25, is identically

$$\sum X_i H_i^{l} + \Delta H_{\mathrm{mix}}^{l} = \sum X_i H_i^{g} + \Delta H_{\mathrm{mix}}^{g} \qquad (28)$$

The use of pure constituent heat capacities and of the condition

$$H_i^{l}(T_{g_i}) = H_i^{g}(T_{g_i}) \qquad (29)$$

allows eq 28 to be written as

$$\sum X_i \int_{T_{g_i}}^{T_g} \Delta C_{p_i}\, dT + \Delta H_{\mathrm{mix}}^{l} - \Delta H_{\mathrm{mix}}^{g} = 0 \qquad (30)$$

In eq 30 the ΔC_{p_i} are given by eq 7 and the excess enthalpies of mixing are those of eq 26.

Parallel to the situation for the volume-based tautology, there is no evident basis for the enthalpic tautology to become predictive unless the excess properties of mixing vanish or are negligible. Thus, only for solutions for which in eq 30 it is at least approximately true that

$$\Delta H_{\mathrm{mix}}^{l} = 0 = \Delta H_{\mathrm{mix}}^{g} \qquad (31)$$

does the enthalpic tautology give rise to the relation

$$\sum X_i \int_{T_{g_i}}^{T_g} \Delta C_{p_i}\, dT = 0 \qquad (32)$$

The simplest integrated form of this athermal solution relation arises if the ΔC_{p_i} are taken as temperature-independent and is eq 11. If the ΔC_{p_i} are taken as inversely proportional to temperature, the relation

$$\ln T_g = \frac{\sum X_i \Delta C_{p_i} T_{g_i} \ln T_{g_i}}{\sum X_i \Delta C_{p_i} T_{g_i}} \qquad (33)$$

is obtained.[22] The ΔC_{p_i} in eq 33 are at their corresponding T_{g_i}.

The Three Theories. The tautologies for the compositional variation of glass transition temperatures of eq 8, 19, and 30 are thermodynamic restatements of the continuity of S, V, and H, respectively, at the solution transition. They are tautologies because the solution relations of eq 1, 12, and 25 used to introduce the pure constituent properties are tautologies. Because the continuity of S, V, and H is general for second-order transitions and the solution relations are tautologically correct, eq 8, 19, and 30 are general and equivalent relations for the compositional variation of second-order transition temperatures.

Each tautology reduces to a differential relation of predictive use when the transition difference between the relevant excess properties of mixing vanishes at the transition of the solution. This reduction does not occur for arbitrary solutions and therefore the versions of the tautologies of predictive use, eq 9, 23, and 32 and their integrated forms, are not general. The conditions that give rise to the three predictive theories, in effect restrictions on the behavior of pure constituent properties alone at the solution transition, are connected only by the requirement that they coincide at the extremes of composition, $X_i = 1$, where $T_g \equiv T_{g_i}$. Thus, the three theories are required to be equivalent only for what is in effect the trivial problem, when all predictive relations for T_g vanish identically. Consequently, the predictive entropic, volume-based, and enthalpic theories are both specific and different.

Of practical interest in connection with the prediction of the compositional variation of T_g is whether one of the three conditions associated with a predictive theory is appropriate in some generality for real solutions. The assumption of random mixing is widespread, almost general, in solution theory, whereas it is not usual to assume that excess volumes or heats of mixing vanish. On this basis, the entropic predictive theory would seem a priori to be of the widest use. This said, it is clear from eq 9 and 32 that there will be problems for which the predictions of the entropic and enthalpic theories may differ little. As among other things the integration of these relations is approximate, the use of one or the other of these two theories might then seem to be largely a matter of choice. However, quantitative considerations aside, the use of the enthalpic theory would be disjoint with the usual assumptions of solution theory and the expected nature of real solutions. Whichever is used, these and indeed all three predictive theories are essentially different.

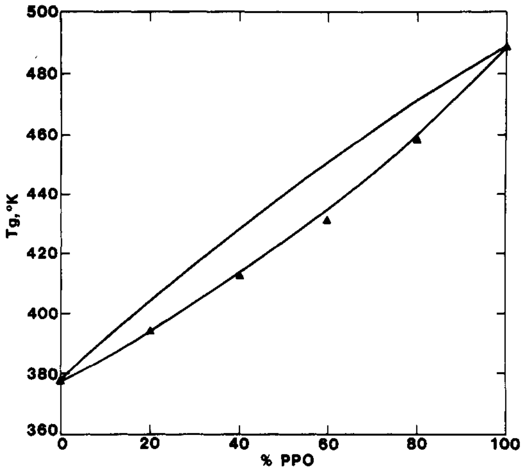

Figure 1. Calculated and observed values of T_g for PS/PPO blends vs. mass percent of PPO. The lower curve is the prediction of the entropic theory in the form of eq 10. The upper curve is the prediction of the volume-based theory in the form of eq 24. Experimental values of T_g reported by Fried[25] are indicated as triangles. Data for the calculations: T_{g_i} from Fried;[25] ΔC_{p_i} from Fried;[25] $\Delta(V_i\alpha_i)$ from Richardson and Savill[26] (PS) and Jauhiainen[27] (PPO).

In principle, the difference between the predictions of the volume-based theory and of either the entropic or enthalpic theories may lie anywhere between severe and negligible. No a priori statement other than this is certain. It is instructive though to compare predicted and observed values of T_g for blends of polystyrene (PS) with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), as these are in several essential respects model miscible blends[1,24] and, also, data are available for the use of both the volume-based theory and the entropic (or enthalpic) theory. As shown in Figure 1 the entropic theory gives good agreement with the observed dependence of T_g on composition, whereas the theory based on the premise of volume additivity fails to account even qualitatively for this dependence. This does not mean that the difference between the two theories is invariably of this kind, but it does suggest that the volume-based theory ought not to be taken as valid in any generality.

While the three predictive theories are not equivalent, their possible overlap is of interest as it gives rise to connections between pure-constituent glass transition properties. However, the class of solutions for which this occurs is necessarily far more exclusive than that for which any one of the associated theories is valid.

The general condition for all three predictive theories to be valid simultaneously is that

$$T_{g_i} = T_{g_j} \qquad (34a)$$

for all i, j. This is also the condition for the entropic and enthalpic predictive theories to be valid simultaneously. Equation 34a includes the requirement for the volume-based and enthalpic theories of eq 23 and 32 to be consistent,[28]

$$\frac{V_i \Delta\alpha_i}{\Delta C_{p_i}} = \frac{V_j \Delta\alpha_j}{\Delta C_{p_j}} \tag{34b}$$

for all i, j. From eq 34, the simultaneous validity of all three predictive theories, or of the entropic and enthalpic theories, can occur only for the trivial case.

If the volume-based theory and either the entropic or enthalpic theory were to be valid simultaneously, the pressure dependence of the glass transition temperatures of the pure constituents must be related.[1,2,10] These are known to vary widely. Again, this suggests that the predictive volume-based theory is not valid in any generality. There does, though, appear to be one problem for which the excess volumes of mixing of eq 13 are known to vanish and for which the compositional variation of T_g has been accounted for by the entropic theory. For polystyrenes of various molecular weights, the specific volume is known to be well represented as a sum of high polymer and chain end contributions and the effect of degree of polymerization on T_g is calculable from the volume-based[26] and entropic[2-4] theories. Data on the relation between T_g and pressure (to ~7 kbar) for various polystyrenes show that the T_g/P curves are essentially parallel[29] for all molecular weights studied (down to $\bar{M}_n = 4000$), consistent with an approximate relation from the simultaneous validity of the two theories.[2,10]

The remarks of this section bear on the suggestion by Goldstein that because the three predictive theories cannot be valid simultaneously the thermodynamic theory is incorrect. The implicit basis of this suggestion is that the predictive theories can be treated as if they were general and equivalent. This is entirely incorrect. Indeed, it is precisely because the theories are neither general nor equivalent that the conditions of their equivalence should not be generally met but rather should be valid only for certain extremely restrictive classes of solutions.

Final Remarks

The excess properties of mixing of the thermodynamic theory for the compositional variation of glass transition temperatures are unique, phase-consistent quantities. General relations of the theory derivable from the entropy, volume, and enthalpy are equivalent but tautological. A consequence is an exact compensation of the transition behavior of the excess properties of mixing and their corresponding pure-constituent sums. The predictive versions of the tautologies are neither general nor equivalent. There are then three specific and different theories for the prediction of the compositional variation of T_g. The "mixing" relations of these are all approximate.

On fairly general grounds, the entropic predictive theory would seem to be of wider a priori applicability than either the volume-based or enthalpic theories. Because the three predictive theories are specific and different, their overlap cannot be at all general and conditions associated with this are of lesser validity than any of the associated theories.

The basis of the thermodynamic theory for the compositional variation of T_g is straightforward and readily comprehensible and does not require a knowledge of the molecular mechanism of the glass transition. The theory provides a simple and convenient method of accounting in some generality for the relation between the T_g of various solutions and the glass transition temperatures of the pure constituents. The need for relations that are both predictive and fairly general means that the theory is heuristic. In addition, the predictive relations are approximate. Quite apart from these points there is the question of the relation of the glass transition itself to an Ehrenfest transition of second order. For the present purpose it seems sufficient to say that the broad similarities between the two, the simplicity of the thermodynamic model, and the overall degree of success enjoyed by the predictive theory make the formal parallel drawn here useful. Nevertheless, even for the formal tautologies there is a heuristic element in the relation of the thermodynamic equations to the problem of the actual compositional variation of T_g.

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(13) See, for example: Callen, H. B. *Thermodynamics*; Wiley: New York, 1962.
(14) To illustrate this, consider the example of a binary solution at a temperature T, where $T_{g_1} < T < T_{g_2}$. Goldstein's[10] "alternative definition" gives that

$$\Delta S_{mix}{}^{g} = S^{g} - (X_1 S_1{}^{l} + X_2 S_2{}^{g})$$

which, in eq 1b (for which this quantity is supposed to be the excess entropy of mixing), gives the result

$$S^{g} = S^{g} + X_1(S_1{}^{g} - S_1{}^{l})$$

This internal contradiction is an explicit demonstration that the "alternative definition" is incompatible with the self-consistency of eq 1b.
(15) See, for example: Sanchez, I. C. In *Polymer Blends*; Paul, D. R., Newman, S., Eds.; Academic: New York, 1978; Vol. 1.
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(17) ten Brinke, G.; Karasz, F. E.; Ellis, T. S. *Macromolecules* **1983**, *16*, 244. Ellis, T. S.; Karasz, F. E.; ten Brinke, G. *J. Appl. Polym. Sci.* **1983**, *28*, 23. Ellis, T. S.; Karasz, F. E. *Polymer* **1984**, *25*, 664.
(18) Wunderlich, B. *J. Phys. Chem.* **1960**, *64*, 1052.
(19) The constant of proportionality in the derivation of eq 11 directly from eq 9 is for each pure constituent the product of T_{g_i} and the corresponding value of ΔC_{p_i}. In addition to being derivable directly from eq 9 in the manner mentioned, eq 11 also arises as a linearized version of eq 10.[5,9]
(20) A complication in the comparison of theory and experiment quite aside from those already mentioned is the use of different experimental conventions to establish T_g. This, in conjunction with the broadening of the glass transition of the solution with respect to the pure constituents, could of itself give rise to a difference between calculated and observed values of T_g.[5]
(21) Thus:[10] "If, for example, V is continuous and ΔV_{mix} is not, then the remaining contributions to V must also possess a discontinuity at T_{gm}, and of equal magnitude and opposite sign to the discontinuity in ΔV_{mix} in order to cancel exactly the bad behavior of ΔV_{mix}. It is hard to believe in the reality of this effect."
(22) Equation 33 can be simplified further by reuse of the assumed relation between the ΔC_{p_i} and T and the assumption that the constant of proportionality is the same for all pure constituents, to give

$$\ln T_g = \sum X_i \ln T_{g_i} \tag{R1}$$

Similarly, eq 11 in the entropic derivation can be rewritten as the Fox relation[23]

$$1/T_g = \sum X_i / T_{g_i} \tag{R2}$$

(23) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.

(24) Wignall, G. D.; Child, H. R.; Li-Aravena, F. *Polymer* **1980**, *21*, 131.
(25) Fried, J. R. Ph.D. Dissertation, University of Massachusetts, 1976.
(26) Richardson, M. J.; Savill, N. G. *Polymer* **1977**, *18*, 3.
(27) Jauhiainen, T.-P. *Makromol. Chem.* **1982**, *183*, 935.
(28) Since eq 34a is valid at arbitrary pressure, *P*,

$$dT_{g_i}/dP = dT_{g_j}/dP \qquad (R3)$$

for all *i*, *j*. From the entropic Ehrenfest relation[13] for the generic pure constituent and eq 34a, eq R3 gives eq 34b.
(29) Takamizawa, M.; Karasz, F. E., unpublished results of high-pressure differential thermal analysis studies of polystyrenes of various molecular weights.

Notes

Chain Propagation/Step Propagation Polymerization. 1. The Polymerization of Ethylene Oxide with an Acetal-Masked Initiator

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Structure control in copolymer synthesis is a continuing challenge for the polymer chemist, a situation that certainly holds true in the synthesis of segmented copolymers by conventional step polymerization techniques. Rarely does one attain a narrow molecular weight distribution for both segments within such copolymers, though this very goal is actively sought by at least two other research groups today.[1,2] In this research we are attempting the synthesis of highly regular segmented copolymers, i.e., those with narrow molecular weight distributions within each segment, by combining chain and step propagation procedures into one synthetic scheme. The thrust of this synthetic strategy focuses on synthesizing a highly regular telechelomer (a high molecular weight monomer) by anionic polymerization that in turn is converted into a copolymer of high molecular weight by step polymerization techniques. Figure 1 depicts the approach as it applies to segmented copolymers.

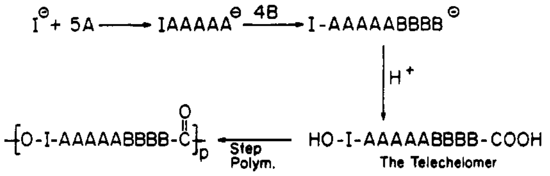

Figure 1. Illustration for chain/step polymerization using 5 "A" units and 4 "B" units.

Let "A" represent the repeat unit within one segment and "B" the repeat unit within the other segment. The initiator, "I", contains a masked functionality that will be used later in step polymerization. Anionic (chain) initiation and polymerization leads to a monodisperse segment of monomer "A". Then either monomer "B" can be added directly or the nucleophilicity of the anion "A" can be altered prior to the addition of the second monomer to facilitate the formation of a monodisperse segment of "B". This new anion, the "B" anion, is then quenched by using chemistry that removes the mask from the initiator, thus creating the desired telechelomer, which can be rigorously purified at this point in the synthetic scheme, followed by mild condensation (step) polymerization to high polymer.

This methodology could be applied to a variety of "A" and "B" monomers to obtain a series of highly regular segmented copolymers containing segments of narrow molecular weight distributions. If the two segments are incompatible, the polymers will exhibit good phase separation and the surface of the polymer will be richer in the segment that has a lower surface energy. Proper selection of monomers, therefore, will lead to polymers having controlled surface properties such as biocompatibility, adhesion, and weathering. If one segment is hard and the other is soft, the segment lengths could be varied to obtain thermoplastic elastomers having good mechanical properties. The surface and mechanical properties of these copolymers could then be compared with those of ABA and AB block copolymers.

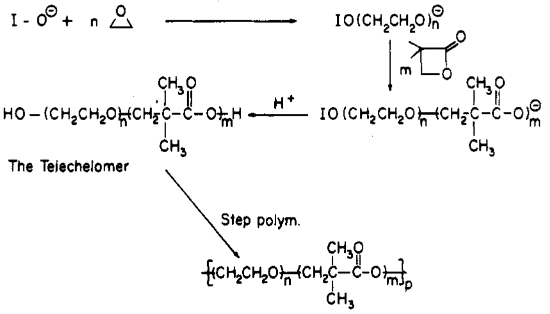

Figure 2. Chain/step synthesis of poly(oxyethylene-*co*-pivalolactone).

We have selected ethylene oxide (EO) and pivalolactone (PVL) as our first monomer pair. A general description of the chemistry used is shown in Figure 2. A masked initiator, I–O$^-$K$^+$, anionically polymerizes ethylene oxide, and the resulting anion is reacted with pivalolactone (PVL) to give a polymeric anion still containing the masked initiator fragment. The product is then acid hydrolyzed to give an oxyethylene–pivalolactone telechelomer, which on step polymerization will give the segmented copolymer.

In this paper we describe the chemistry needed to synthesize an acetal-masked potassium alkoxide initiator for the chain polymerization aspect of the research, and we describe how this acetal-masked initiator readily polymerizes ethylene oxide while keeping the mask in place. Acetal-masked lithioalkoxides have been previously reported by Schulz et al. for butadiene polymerization[3] and by Lefebvre for hexamethylcyclotrisiloxane polymerization.[4]

Experimental Section

Acetaldehyde 3-Chloropropyl Ethyl Acetal (1) and Its Organolithium Salt 2. The chloroacetal 1 was prepared according to the procedure of Eaton et al.,[5] using 3-chloro-1-propanol

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