imply that the aggregate states consisting of a large size were removed by filtration. The intensity of light scattering can be affected significantly by a small amount of large aggregates. At the light scattering measurement for micelle formation in polydispersed copolymer, this effect may become nonnegligible.

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Glass Temperature Mixing Relations and Thermodynamics

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ABSTRACT: The view of Couchman that the following equation for the glass temperature of a mixture of polymers

$$\ln T_{gm} = \frac{X_1 \Delta C_{p1} \ln T_{g1} + X_2 \Delta C_{p2} \ln T_{g2}}{X_1 \Delta C_{p1} + X_2 \Delta C_{p2}}$$

can be justified from a purely thermodynamic standpoint is disputed. The reasoning behind this claim is shown to be based on an inappropriate definition of the entropy of mixing when either or both pure polymers are in their glassy states. An alternative definition of ΔS_{mix} having a sounder physical basis does not lead to any prediction of T_{gm}. The above equation has also been derived from the standpoint of the Gibbs–DiMarzio *molecular* theory of the transition, and to the extent that it successfully predicts T_{gm} it supports molecular theories that attribute a special importance to the configurational entropy.

Introduction

In a series of papers in this Journal[1-3] and elsewhere[4-7] Couchman has developed a thermodynamic approach for predicting the glass temperatures of various polymer mixtures, based on a thermodynamic discussion of the effect of composition on the glass transition by him and Karasz.[8] This approach bypasses any consideration of molecular theories of the transition (such as the Gibbs–DiMarzio entropy theory[9] or free volume theories,[10-12] although molecular considerations are used to estimate the values of certain thermodynamic quantities.

Additional developments depend on what is assumed about the continuity of the changes of first-derivative thermodynamic properties on mixing. If it is assumed that ΔS_{mix}, ΔH_{mix}, and ΔV_{mix} are continuous through the transition, three separate equations for T_{gm}, the glass temperature of a mixture, are obtained (for simplicity, ΔC_p and $\Delta\alpha$ are taken to be temperature independent):

Entropy S:

$$\ln T_{gm} = \frac{X_1 \Delta C_{p1} \ln T_{g1} + X_2 \Delta C_{p2} \ln T_{g2}}{X_1 \Delta C_{p1} + X_2 \Delta C_{p2}} \tag{1a}$$

Volume V:

$$T_{gm} = \frac{X_1 V_1^\circ \Delta\alpha_1 T_{g1} + X_2 V_2^\circ \Delta\alpha_2 T_{g2}}{X_1 V_1^\circ \Delta\alpha_1 + X_2 V_2^\circ \Delta\alpha_2} \tag{1b}$$

Enthalpy H:

$$T_{gm} = \frac{X_1 \Delta C_{p1} T_{g1} + X_2 \Delta C_{p2} T_{g2}}{X_1 \Delta C_{p1} + X_2 \Delta C_{p2}} \tag{1c}$$

In the above equations, subscripts 1 and 2 denote properties of the pure polymers, and the subscript m properties of the mixture. T_g is the glass transition temperature, X is the mole fraction, V° is the volume of the pure polymer, and ΔC_p and $\Delta\alpha$ are the discontinuities in the specific heat and thermal expansivity at the respective T_g's.

As Couchman has noted, each of the above equations has been previously given by others on the basis of specific *molecular* theories,[13-16] but Couchman's claim that they follow from purely thermodynamic arguments[19] based on the continuity of ΔS_{mix}, ΔH_{mix}, and ΔV_{mix} at T_g would seem to make molecular considerations irrelevant.

Problems with the Thermodynamic Approach

Couchman has recognized problems with these equations and discussed them in a number of papers.[28] He has noted for example that if both (1b) and (1c) are *simultaneously* true, it would follow that the following relation must hold for any two compatible polymers:

$$\frac{\Delta C_{p1}}{T_{g1} V_1^\circ \Delta\alpha_1} = \frac{\Delta C_{p2}}{T_{g2} V_2^\circ \Delta\alpha_2} \tag{2}$$

This seems to imply a universal value of $\Delta C_p / T_g V^\circ \Delta\alpha$ for *all* polymers, a possibility contradicted by experiment: The quantity in question is a good predictor of dT_g/dP and has been frequently calculated. Observed values range over a factor of 3.[17,18]

An even more serious difficulty would arise if (1a) and (1c) were simultaneously true. For simplicity, if we consider mole fractions X_1 and $X_2 = {}^1/_2$ and further consider a case in which $\Delta C_{p1} = \Delta C_{p2}$, we obtain

$$\ln T_{gm} = \tfrac{1}{2} \ln T_{g1} + \tfrac{1}{2} \ln T_{g2} \tag{1a$'$}$$

$$T_{gm} = \tfrac{1}{2} T_{g1} + \tfrac{1}{2} T_{g2} \tag{1c$'$}$$

In other words eq 1a gives T_{gm} as the geometric mean of T_{g1} and T_{g2}, while eq 1c gives it as the arithmetic mean. This can never occur unless $T_{g1} = T_{g2}$. In short, (1a) and (1c) are actually mathematically incompatible.

Couchman notes that when experimental values of ΔC_p and $\Delta\alpha$ are used in eq 1a–c the predicted T_g's differ. He finds eq 1a the most successful and applies it to many kinds of systems. He suggests that the assumption of continuity for ΔV_{mix} and ΔH_{mix} at T_{gm} will not generally be satisfied, but that for ΔS_{mix} is, on molecular grounds, less likely to be violated, and in polymer systems at least is sufficiently small so that any discontinuity in its value may be neglected even if it were to have a discontinuity at T_{gm}.[1]

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His view is that the assumption of a regular solution is sufficient to ensure continuity of ΔS_{mix}, but not of ΔH_{mix} and ΔV_{mix}, "For random mixtures, the excess enthalpy and volume are generally finite and change discontinuously at the glass transition. The excess entropy of mixing, finite except for high polymers (for which it is vanishingly small), is by contrast essentially continuous as the glass transition is traversed."[7]

The possibility of discontinuities of ΔH_{mix} and so on at T_g raises some conceptual problems that need further discussion. Discontinuities in second-derivative properties are of course characteristic of the transition, and the molecular basis of such discontinuities is qualitatively understood. On the other hand, the continuity of the total S, H, or V at T_g is taken for granted: after all, at T_g the liquid and the glass are the *same* state—the distinction depends on what the observer does next. Further, it is not implausible that these first-derivative properties can be represented as a sum of contributions from various sources. In particular the S, H, or V of a mixture must tautologicaly be representable as a sum of pure component properties and a mixing term.

But what possible molecular explanation could there be for a discontinuity in ΔH_{mix} or ΔV_{mix} at T_g? None has so far been offered.

When the hypothesized discontinuity in ΔH_{mix} or ΔV_{mix} is considered together with the known continuity of H and V through the transition, a worse problem emerges. If, for example, V is continuous and ΔV_{mix} 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 such an effect.

If the equations (1) were to be interpreted as predictions from *molecular* theories, and if any one of them fails, it would be taken to reflect on the theory from which it was obtained. If, however, the equations are really consequences of thermodynamics, any failure requires a different kind of analysis.

The view I will present in this paper is that the condition of continuity on ΔS_{mix} at T_{gm}, plausible as it sounds, will not in general be satisfied. There are likely to be discontinuities in ΔS_{mix}, ΔH_{mix}, and ΔV_{mix} at T_{gm}, which are artifacts of the particular definitions of these quantities used by Couchman. My conclusion is that there is no purely thermodynamic rationale for equations (1), and to the extent that each of them is confirmed or disconfirmed, so are the molecular theories from which they are derived.

Definitions of Property Changes on Mixing

Figure 1 gives a schematic representation of the behavior of the molar entropy–temperature relationships for two pure polymers and of an equimolar mixture. For simplification, the entropy–temperature relationships for liquid and glassy states are drawn as straight lines: all three liquids are assumed to have a single slope (lines 1L, 2L, and ML) and so are all three glasses (lines 1G, 2G, and MG). Two possible values for the T_g of the mixture are considered: T_{gm}, which is chosen to satisfy (1a), and T_{gm}', which is chosen to lie *below* both T_{g1} and T_{g2}, for purposes of illustration. It is not claimed that this is a plausible state of affairs in compatible polymers. The dashed line labeled PL represents the entropy of a system composed of $^1/_2$ mol of each of the two pure liquid polymers, as yet unmixed. (1L, 2L, and PL are extrapolable below any or all of the T_g's.) The dashed line PG represents the entropy of a system composed of $^1/_2$ mol of each of the two pure glassy polymers. The polymers are assumed to have undergone their glass transitions at their respective T_g's, but their subsequent behavior is defined by extrapolations of the lines 1G and 2G. The curves PL and PG cross at that temperature at which the liquid and glass entropies of the equimolar unmixed system are equal, i.e., at a temperature T_c such that

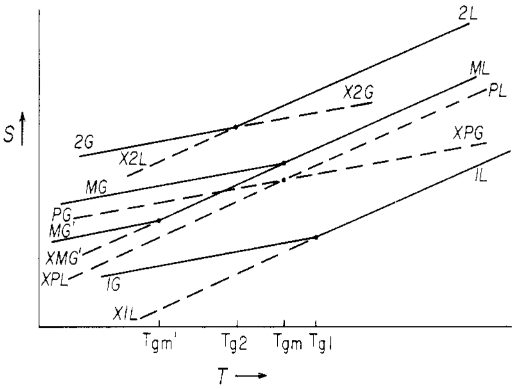

Figure 1. Entropy–temperature relationships. The lines 1L–1G and 2L–2G give the entropy–temperature relationships for two pure polymers undergoing their glass transition at T_{g1} and T_{g2}. X1L, X2G, and X2L represent extrapolations needed for the calculation of entropies of mixing as defined by Couchman. The lines PL and PG describe the entropy of a system composed of $^1/_2$ mol of each of the two pure polymers, *unmixed*. The behavior of the mixed system is denoted by the lines ML, MG, and MG′, the latter two associated with two possible values, T_{gm} and T_{gm}', for the glass temperature of the mixture. See text for further details.

$$\ln T_c = \frac{X_1 \Delta C_{p1} \ln T_{\text{g1}} + X_2 \Delta C_{p2} \ln T_{\text{g2}}}{X_1 \Delta C_{p1} + X_2 \Delta C_{p2}} \tag{3}$$

The entropy of mixing of liquid polymers, as defined by Couchman, is given by the vertical distance from the line PL to the line ML.

$$\Delta S_{\text{mix}}[1] = S_{\text{mix}}(1) - X_1 S_1{}^\circ(1) - X_2 S_2{}^\circ(1) \tag{4}$$

where S_{mix} = the entropy of 1 mol of the mixture. This relation is the conventional definition of the mixing entropy and presents no problems. Couchman uses it at T_{gm}, which requires an extrapolation of the line 1L below T_{g1}, but this appears a reasonable procedure.

Couchman defines the entropy of mixing of glassy polymers (for the special case $X_1 = X_2 = {}^1/_2$) by the relation

$$\Delta S_{\text{mix}}(\text{gl}) = S_{\text{mix}}(\text{gl}) - \tfrac{1}{2} S_1{}^\circ(\text{gl}) - \tfrac{1}{2} S_2{}^\circ(\text{gl}) \tag{5}$$

It is obvious that at T_{gm}, wherever it may occur,

$$S_{\text{mix}}(1) = S_{\text{mix}}(\text{gl}) \tag{6}$$

because glass and liquid are, of course, the *same* state at T_{gm}.

In Figure 1, as noted earlier, the dashed line PG gives the entropy of a system composed of $^1/_2$ mol of each of the two pure polymers in the glassy state, each having undergone its transition to this state at its own T_g. Equation 5 implies that $\Delta S_{\text{mix}}(\text{gl})$ is given by the vertical distance, at any temperature, from MG, which gives the entropy of the mixture in the glassy state, to the line PG.

The assumption of continuity of ΔS_{mix} at T_{gm} implies therefore that T_{gm} must coincide with the temperature T_c at which PG and PL cross, as this is the only temperature where the relation

$$\Delta S_{\text{mix}}(\text{gl}) = \Delta S_{\text{mix}}(1) \tag{7}$$

can be satisfied.

It can be shown easily that on combining eq 4–7, eq 1a results. Couchman notes that even if eq 7 is not satisfied and ΔS_{mix} is discontinuous at T_{gm}, provided both $\Delta S_{\mathrm{mix}}(\mathrm{l})$ and $\Delta S_{\mathrm{mix}}(\mathrm{gl})$ are so small they can be neglected, eq 1a follows from eq 4–6 alone. He gives plausible reasons for believing that $\Delta S_{\mathrm{min}}(\mathrm{l})$ is small in mixtures of high polymers[1] and concludes that a discontinuity in this small quantity will not alter the vaidity of eq 1a.

In Figure 1 we have shown a finite $\Delta S_{\mathrm{min}}(\mathrm{l})$. This is not necessary: if $\Delta S_{\mathrm{mix}}(\mathrm{l})$ were truly negligible, line ML would coincide with line PL.

We note however that even if $\Delta S_{\mathrm{mix}}(\mathrm{l})$ were negligible, $\Delta S_{\mathrm{mix}}(\mathrm{gl})$ calculated at T_{gm}, the glass temperature of the polymer mixture, is strongly dependent on T_{gm} itself. If T_{gm} does not happen to coincide with T_{c}, the temperature at which PG and PL cross, $\Delta S_{\mathrm{mix}}(\mathrm{gl})$ at T_{gm} may be quite large.

The figure shows what would be the case if the glass temperature of the mixture were lower than that given by eq 1a, i.e., at T_{gm}'. $\Delta S_{\mathrm{mix}}(\mathrm{gl})$ at T_{gm}' is large and negative. If the glass temperature were much higher than given by eq 1a, $\Delta S_{\mathrm{mix}}(\mathrm{gl})$ would be large and positive. In either case the entropy S_{mix} of the polymer mixture would be continuous at its glass temperature, just as it is at the temperature given by eq 1a (T_{gm} in Figure 1).

It is my view that the "problem" of the discontinuity of ΔS_{mix} arises from the manner in which it was defined (eq 5). While purely as a definition eq 5 cannot be criticized, when we attribute to ΔS_{mix} defined by it the ordinary properties of an entropy of mixing with which we are familiar, and about which we have some intuitive notion, we can be led seriously astray.

That the "discontinuity" in ΔS_{mix} at T_{gm} *must* occur in some real systems is shown by the fact that not every system examined as in perfect agreement with eq 1a, even though it does offer better overall agreement with experiment than other equations for T_{gm}. But thermodynamics correctly applied does not admit of exceptions.

On writing for either liquid or glassy phases relations of the form

$$L_{\mathrm{mix}} = X_1L_1{}^{\circ} + X_2L_2{}^{\circ} + \Delta L_{\mathrm{mix}}$$

(where $L = S$, H, or V), we can see the origin of the mysterious simultaneous compensating discontinuities referred to earlier. By insepection of the figure we can verify that $X_1L_1{}^{\circ}(\mathrm{l}) + X_2L_2{}^{\circ}(\mathrm{l})$ can equal $X_1L_1{}^{\circ}(\mathrm{gl}) + X_2L_2{}^{\circ}(\mathrm{gl})$ only at one particular temperature and not otherwise. Unless this temperature fortuitously coincides with T_{gm}, the glass temperature of the mixed system, there will be a discontinuity in $X_1L_1{}^{\circ} + X_2L_2{}^{\circ}$ at T_{gm}, which must be compensated for by a discontinuity in ΔL_{mix} to maintain the undisputed continuity of L itself.

I have thus shown that the "discontinuities" of ΔS_{mix}, ΔH_{mix} or ΔV_{mix} at T_{gm} violate neither thermodynamics nor experimental reality.

The conclusion is that the claimed thermodynamic basis for eq 1a is not valid. It is T_{gm} that determines $\Delta S_{\mathrm{mix}}(\mathrm{gl})$ rather than the reverse. The experimental success of eq 1a is thus support for molecular theories of the transition that assign a special role to entropy.

An Alternative Definition

Having expressed the view that Couchman's definition of $\Delta S_{\mathrm{mix}}(\mathrm{gl})$ is misleading, I would like to offer an alternative definition, which I feel has a more physical basis and has the further advantage of avoiding any discontinuities of ΔS_{mix} at glass transition temperatures.

I define ΔS_{mix} (for $X_1 = X_2 = {}^1/_2$) at any temperature T as the ΔS for the process ${}^1/_2$ mol of polymer 1 at T + ${}^1/_2$ mol of polymer 2 at $T \rightarrow$ 1 mol of polymer mixture at T, where each of the polymer systems is in whichever state, liquid or glass, that is the usual state at T: polymer 1 is liquid if $T > T_{\mathrm{g}}$ and glassy if $T < T_{\mathrm{g1}}$ and so on.

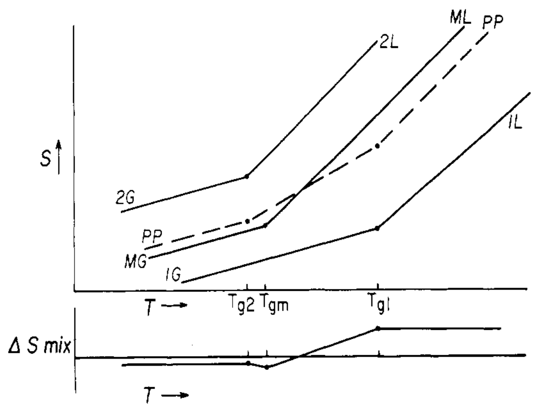

Figure 2. Alternative definition of entropy of mixing. In the upper graph the entropies of polymer 1, polymer 2, an unmixed system composed of ${}^1/_2$ mol of each of the polymers, and the mixed system are shown as 1L–1G, 2L–2G, PP, and ML–MG, respectively. ΔS_{mix} is the vertical distance from PP to ML–MG and is shown in the bottom graph. It has no discontinuities, but there are three discontinuities in slope at T_{g1}, T_{gm}, and T_{g2}.

The entropies of the three polymer systems are represented schematically in Figure 2. The dashed line PP represents the dependence of the entropy on temperature for a system composed of ${}^1/_2$ mol of each of the two pure polymers. Notice that PP shows two discontinuities in slope at the T_{g}'s of the pure polymers, but no discontinuity in the entropy itself. ΔS_{mix} is given by the vertical distance between the entropy of the mixture (ML above T_{gm} and MG below it) and PP. ΔS_{mix}, according to this definition, has three discontinuities in its slope, but is itself continuous everywhere. The entropy S_{mix} of the mixture is, as usual, continuous at T_{gm}. In the particular situation portrayed in Figure 2, ΔS_{mix} becomes negative at low temperatures; this should not be a cause for alarm. It is a direct consequence of the departure of our systems from (metastable) equilibrium below the glass temperature of any of the components.

Conclusions

The claim that there is a purely thermodynamic basis for the mixing equation

$$\ln T_{\mathrm{gm}} = \frac{X_1\Delta C_{p1} \ln T_{\mathrm{g1}} + X_2\Delta C_{p2} \ln T_{\mathrm{g2}}}{X_1\Delta C_{p1} + X_2\Delta C_{p2}}$$

is disputed. The reasoning behind this claim is shown to be based on an inappropriate definition of ΔS_{mix} when the products or the reactants are in their glassy states. To the extent that this equation is successful, it provides experimental support for those molecular theories of the glass transition that assume a special importance for the configurational entropy.

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Properties of Partially Cured Networks. 2. The Glass Transition

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ABSTRACT: The increase of the glass transition temperature during the isothermal cure of a model network formed by the reaction of α,ω-dihydroxypoly(propylene oxide) with tris(4-isocyanatophenyl) thiophosphate has been investigated. It is shown that the reaction proceeds first under kinetic control and then under diffusion control upon which is superimposed an intramolecular reaction beyond the gel point. Loop formation occurring during the intramolecular reaction leads to a decrease in the rate of the T_g increase due to plasticization. The dependence of the T_g change on the degree of cure is treated by a WLF approach. The diffusion-controlled part of the cure of the model network investigated and also that of two epoxy resins follow a master curve. Broadening of the glass transition in the model network is attributed to the influence of increasing hydrogen bonding between urethane NH and ether oxygen groups.

Introduction

The measurement of T_g during an isothermal cure is often a difficult task. This is due to the fact that at low temperatures curing systems often vitrify at low conversion and then the reaction is more or less stopped.[1] On the other hand, at high curing temperature reactions are often so fast that T_g measurements are not possible during the cure. However, T_g change accompanying the cure of such systems has been measured by reacting the systems at different temperatures and determining the conversion at which vitrification occurs.[2–4] The T_g increase during isothermal cure cannot be investigated in that way and the method works only if the curing reaction really is stopped by the vitrification.

The investigation of processes occurring during isothermal cure over the whole range of conversion is possible with certain systems.[5] These systems must cure slowly even at temperatures above the final network T_g. With a knowledge of the curing kinetics the T_g increase with degree of reaction can be correlated with conversion.

In our previous paper[6] we described the kinetics of a slowly curing model network-forming system. The use of model networks in investigations of partially cured systems is desirable because of the ease with which their well-defined structures can be related to their properties. This will be demonstrated in the present work.

Experimental Section

Materials. The system is the same which has been used in our previous work.[6] It consists of α,ω-dihydroxypoly(propylene oxide) with molecular weight 1000 (PPO1000) obtained from Aldrich Chemical Co. and tris(isocyanatophenyl) thiophosphate (triisocyanate) obtained from Mobay Corp.

Analytical data have been given elsewhere as well as methods for purification of prepolymer and cross-link agent and the synthetic procedure for the network formation.[6]

Calorimetry and Sample Preparation. All glass transition temperatures and the incremental change in heat capacity at T_g were measured calorimetrically using a Perkin-Elmer differential scanning calorimeter, DSC-2. Heating rate was 20 °C/min. The samples used have been prepared by transferring a drop (about 7–10 mg) of the clear curing mixture to a Perkin-Elmer aluminum sample pan for liquid samples. The sample was kept at −80 °C for about 15 min before being placed in the DSC. Once there, it was not removed until the end of the cure.

The T_g was measured after the sample was cooled at the fastest rate to between 180 (in the early stages of cure) and 210 K where it was allowed to remain for 10–15 min. Each measurement was repeated four or five times. After the measurements, the sample was heated to the curing temperature, 303 K, within ~30 s. Measurement of the width of the glass transition represents an average of 4–5 determinations and is defined as the temperature interval between the intersection of the line drawn through the inflection of the heat capacity change at the transition with the lines drawn through the extrapolated base lines before and after the transition.

Results and Discussion

Change in $\Delta C_p(T_g)$ and Width of the Glass Transition. Figure 1 shows T_g vs. time for the cure of PPO1000–triisocyanate at 303 K. Figure 2 shows some of the corresponding DSC traces.

Two features are easily observed. First, $\Delta C_p(T_g)$ decreases with increasing T_g and, second, the glass transition becomes broader as cure proceeds. A decrease in $\Delta C_p(T_g)$ with increasing T_g is expected due to different slopes for C_p(glass) and C_p(rubber).[5]

Broadening of the glass transition with increasing cross-link density has been observed in divinylbenzene cross-linked polystyrene prepared by radical copolymerization.[7] This has been attributed to a broadening of the molecular weight distribution of the chains between cross-link points. However, in network formation proceeding through end-linking reactions the distribution of molecular weights between cross-links is determined by the prepolymer molecular weight distribution and does not change. Data of the diglycidyl ether of bisphenol A type prepolymers cured with phthalic anhydride show no glass transition broadening with increasing cross-link density.[5] The explanation for the behavior observed here becomes obvious when the data are plotted against conversion (Figure 3). Up to very high conversions a linear relationship is found ($\Delta T = 0.112(\text{conversion }(\%)) + 5.4$). The only quantity increasing linearly with conversion is the concentration of urethane groups, i.e., of NH groups. As has been shown,[8] the urethane NH group forms hydrogen

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