in the configurational states between the liquid and the glass. His conclusion is thus in essential agreement with the results obtained in this work.

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A Classical Thermodynamic Discussion of the Effect of Composition on Glass-Transition Temperatures

P. R. Couchman and F. E. Karasz*

Materials Research Laboratory and Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003.

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ABSTRACT: The effect of composition on glass-transition temperatures is considered from a classical thermodynamic viewpoint, providing two fundamental relations for the effect.

Gordon, Rouse, Gibbs, and Risen[1] have recently treated the composition dependence of some glass-transition properties on the basis of the configurational entropy theory of glass formation.[2,3] Our purpose is to complement and extend fundamental aspects of their development by considering the application of classical thermodynamics to the effect of mixing on the glass transition, an amplification of our previous remarks on the topic.[4]

For formal purposes we treat the glass transition as an Ehrenfest second-order transition[5] and use the characteristic continuity and discontinuity conditions of such phenomena, together with some simple explicit assumptions and approximations, to provide relations expressing the glass-transition temperature T_g of the mixture in terms of the glass-transition temperatures T_{g_1} and T_{g_2} of the individual pure components. Explicitly the latter two transitions are replaced in the mixture by the single transition at temperature T_g, as would, for example, occur in polymer–plasticizer and compatible polymer–polymer and other systems. This discussion therefore does not purport to predict whether or not a single transition is observed but is rather a phenomenological treatment applicable to compatible systems. There are two fundamental relations for the effect of composition on T_g, one arising from the entropy continuity condition (at T_g) and the other from the volume continuity condition. These relations are derived in turn. For simplicity we consider a two-component system (the formalism we present is easily extended to systems with a large number of components).

The respective mole fractions of the two components in the system are denoted as x_1 and x_2 and the molar entropies of these pure components are designated in turn as S_1 and S_2. The molar entropy, S_{tot}, of the mixed system may be written generally as

$$S_{tot} = x_1 S_1 + x_2 S_2 + \Delta S_{mix} \tag{1}$$

where ΔS_{mix} includes any and all excess entropy changes (conformational, thermal, etc.) associated with mixing the two components. The behavior of ΔS_{mix} at T_g is central to the derivation of the final relation for the composition dependence of glass-transition temperatures. We start by considering the

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simplest case, when the excess entropy of mixing is solely conformational.[6] Since the composition of the system is fixed it then follows that ΔS_{mix} is continuous at T_g. More generally, when there are nonconformational contributions to the excess entropy of mixing, it would seem reasonable to suppose that at least in certain circumstances the character and extent of specific interactions may be largely unchanged at T_g.

Let $S_1°$ and $S_2°$ denote pure component molar entropies at respectively T_{g_1} and T_{g_2} and let C_{p_1} and C_{p_2} denote the molar heat capacities of these components. The part of the total molar entropy excluding ΔS_{mix} is designated $\bar{S}_{\text{mix}}$ and may be written generally as

$$\bar{S}_{\text{mix}} = x_1 \left\{ S_1° + \int_{T_{g_1}}^{T_g} \frac{C_{p_1}}{T} \, \mathrm{d}T \right\} + x_2 \left\{ S_2° + \int_{T_{g_2}}^{T_g} \frac{C_{p_2}}{T} \, \mathrm{d}T \right\} \quad (2)$$

A relation of this form is obtained for both the glassy and rubbery states, though, of course, C_p undergoes a finite discontinuity at the transition. Since $S_1°$ and $S_2°$ are continuous at respectively T_{g_1} and T_{g_2}, the continuity of $\bar{S}_{\text{mix}}$ at T_g and the approximation that the transition isobaric heat capacity increments ΔC_{p_1} and ΔC_{p_2} are temperature independent provides the expression

$$\ln \frac{T_g}{T_{g_1}} = \frac{x_2 \Delta C_{p_2} \ln (T_{g_2}/T_{g_1})}{x_1 \Delta C_{p_1} + x_2 \Delta C_{p_2}} \quad (3)$$

If the further approximation $\ln (1 + y) \approx y$ is valid, eq 3 may be rearranged as

$$T_g \approx \frac{x_1 T_{g_1} + (1 - x_1)(\Delta C_{p_2}/\Delta C_{p_1}) T_{g_2}}{x_1 + (1 - x_1)(\Delta C_{p_2}/\Delta C_{p_1})} \quad (4)$$

and is formally identical to an equation derived by Gordon et al.[1] from the Gibbs–DiMarzio theory of the glass transition and to well-known empirical expressions for the composition dependence of T_g.

Derivation of a relation for the composition dependence of T_g from the volume continuity condition proceeds in a manner essentially similar to the development of eq 3 and leads to an equation similar in form to eq 4 or, equivalently, to

$$T_g = \frac{\phi_1° \Delta\alpha_1 T_{g_1} + \phi_2° \Delta\alpha_2 T_{g_2}}{\phi_1° \Delta\alpha_1 + \phi_2° \Delta\alpha_2} \quad (5)$$

The volume fractions $\phi_1°$ and $\phi_2°$ are defined in terms of the molar volumes $V_1°$ and $V_2°$ evaluated at respectively T_{g_1} and T_{g_2}; the transition isobaric volume expansivity increments $\Delta\alpha_1$ and $\Delta\alpha_2$ are derived from the definition $\alpha_i \equiv 1/V_i° \, (\partial V_i/\partial T)_p$. Only if these conditions are met is eq 5 obtained from the classical thermodynamic theory. This relation is, for example, formally identical to that obtained from the simplest use (i.e., linear additivity) of the free volume hypothesis of glass formation; however, it is important to note that the interpretation of the volume fractions and the expansivity increments differ in the two treatments. Specifically, in the free volume treatment the volume fractions are evaluated at T_g and the expansivities are defined in the more usual manner $\alpha_i \equiv 1/V_i \, (\partial V_i/\partial T)_p$.

Aside from the suitability of pertinent approximations (see later) the validity of eq 3–5 requires only that the transition be treated formally as a second-order Ehrenfest transition and that the appropriate excess mixing parameters (ΔS_{mix} and ΔV_{mix}) are continuous at T_g. Consequently, these relations are independent of any molecular theory or interpretation of the glass transition. Further, the derived relations indicate unambiguously that there are two different but apparently rather similar expressions for the composition dependence of T_g.

It is well-known that semiempirical relations formally identical to eq 4 and 5 are not invariably suitable to describe the observed variation of T_g with composition. In the context of the theory we have presented several reasons for such differences to suggest themselves. Insofar as eq 4 is concerned, aside from the previously mentioned possible use of inappropriate weighting factors, two principal sources of discrepancies may arise: (i) the specific approximations leading to eq 4 are unsatisfactory over the relevant temperature ranges, and (ii) ΔS_{mix} is not constant at T_g.

The first-mentioned difficulties may be overcome formally by use of a suitable explicit expression for the temperature dependence of the heat capacities and by retaining the logarithmic functions. For example, if the familiar heat capacity polynomial $C_{p_i} = a_i + b_i T + c_i T^2 + d_i T^3$ is used, the following expression is obtained for T_g:

$$x_1 \left\{ \Delta a_1 \ln \frac{T_g}{T_{g_1}} + \Delta b_1 (T_g - T_{g_1}) + \frac{\Delta c_1}{2} (T_g^2 - T_{g_1}^2) + \frac{\Delta d_1}{3} (T_g^3 - T_{g_1}^3) \right\} + x_2 \left\{ \Delta a_1 \ln \frac{T_g}{T_{g_2}} + \Delta b_2 (T_g - T_{g_2}) + \frac{\Delta c_2}{2} (T_g^2 - T_{g_2}^2) + \frac{\Delta d_2}{3} (T_g^3 - T_{g_2}^3) \right\} = 0$$

The Δ denote transition increments of the various constants. Application of this relation [with the approximation C_p (glass) = C_p (crystal)] to the seven binary mixtures[7,8] considered by Gordon et al.[1] (for the six alcohol mixtures chosen ΔS_{mix} is known to be configurational) predicts values of T_g sensibly indistinguishable from predictions of the conformational entropy theory. It does not, however, follow that such coincidence invariably arises. It is also useful to note that the theory we have presented offers advantages concomitant with the determination and variation of actual rather than fictive temperatures. For example, its use does not require a knowledge of fusion entropies.

If the above-mentioned possible sources of departure between theory and experiment are removed and discrepancies still remain, one would need to consider the possibility and implications of the sensible variation of ΔS_{mix} as the system passes infinitesimally through T_g.

The major possible sources of deviation from eq 5 are: (i) the volume fractions used in the relation may be different from the ϕ_i (this would not seem to be a major possible source of error), separately, the transition isobaric volume expansivity increments may not be well-approximated as constant over the temperature ranges, and (ii) ΔV_{mix} may change at T_g. If volume fraction values are reduced to the appropriate temperatures and $\Delta\alpha_1$ and $\Delta\alpha_2$ are known as functions of temperature, the first-mentioned sources of error may be removed. Any remaining departure between theory and experiment would then need to be considered in the light of a possible change in ΔV_{mix} at T_g.

We have presented an elementary formal and physical discussion of the variation of glass-transition temperature with composition in binary systems, demonstrated that there are two fundamentally different equations for this phenomenon, and discussed possible departures from these equations.

Appropriate topics for subsequent consideration are, for example, the comparison of eq 5 with experimental values of T_g, consistency of the two types of mixing relations [e.g., comparison of the simplest relations, eq 4 and 5, provides the condition

$$\frac{V_2°}{V_1°} \frac{\Delta\alpha_2}{\Delta\alpha_1} = \frac{\Delta C_{p_2}}{\Delta C_{p_1}}$$

subject, of course, to the approximations already introduced], application of the theory to systems in which ΔS_{mix} is not solely conformational, and so forth. This last explicit relation suggests that for systems adhering to Ehrenfest formalism there can be a universal relation for the pressure dependence of pure components, viz., $\mathrm{d}\ln T_g/\mathrm{d}P$ = constant.

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The Influence of Side Groups in Polymer Chain Dynamics. Alternative Comparisons of Viscoelastic Data and Dilute Solution Theory

Barry G. Brueggeman, Michael G. Minnick, and John L. Schrag*

Department of Chemistry and Rheology Research Center, University of Wisconsin, Madison, Wisconsin 53706. *Received September 6, 1977*

ABSTRACT: Extensive high-frequency studies of viscoelastic properties of dilute polymer solutions have been reported by Ferry and associates. Every system examined has shown a finite limiting value η'_∞ for the real part η' of the complex viscosity coefficient η^*, contrary to the predictions of simple bead-spring model theories. Further, η'_∞ is sensitive to the specific side group incorporated in the polymer. Initially the data were fitted with the Peterlin theory which was the only treatment available that predicted a nonzero η'_∞; approximate eigenvalues of the hydrodynamic interaction matrix were used but excellent fits were obtained. Recently an exact solution has been given by Peterlin and Fong; inclusion of exact eigenvalues substantially alters the theoretical predictions so that fits to the data are no longer possible. In addition, more detailed and realistic bead-rod models have been analyzed by Fixman and coworkers; they calculate nonzero values for η'_∞ which are several orders of magnitude smaller than those measured. At present there is no theory which predicts the observed viscoelastic properties, and the physical origin of η'_∞ is not clear. An empirical data modification procedure has been applied to the viscoelastic data in which the high-frequency limiting behavior is subtracted from the measured properties. The modified data plot shapes that results are essentially independent of concentration, molecular weight, and polymer species and correspond to Zimm theory predictions for very small values of hydrodynamic interaction; i.e., a unique master curve shape is obtained by this procedure for all data examined. However, the simple modification apparently does not result in the entire chain dynamics contribution being displayed. A molecular weight dependence of the intrinsic limiting value of η'_∞ appears for polystyrene solutions at molecular weights below 10 000, indicating that up to 100 monomer units may be involved in whatever motions are responsible for η'_∞; side groups may play an important role. Additional experimental evidence on a variety of different molecules as well as a more complete and general theory of chain dynamics will be required in order to understand the role of conformational dynamics in the viscoelastic properties of polymer solutions.

Extensive effective high-frequency studies of the linear viscoelastic properties of dilute polymer solutions have been reported over the last several years by Ferry and collaborators;[1–4] measurements were carried out over a wide effective frequency range utilizing the modified Birnboim apparatus.[5] The systems which have been studied are monodisperse atactic polystyrenes and poly(α-methylstyrenes) of various molecular weights and chain topologies, as well as some poly(2-substituted methyl acrylates) in two chlorinated biphenyl (Aroclor) solvents; all of the polymers examined to date in this laboratory have contained large side groups. The high-frequency regime, which reflects the contributions of fairly local motions to these properties, has been of particular interest since η', the real part of the complex viscosity coefficient η^*, reaches a finite limiting value of η'_∞ which is substantially greater than the solvent viscosity η_s contrary to the predictions of simple bead-spring model theories.[6–8] Here η'_∞ denotes the value of η' for the first high-frequency plateau although there is some evidence for a second plateau at much higher frequencies;[2,9] to this extent the subscript ∞ is somewhat arbitrary. These prior studies showed that η'_∞ is independent of molecular weight for linear polystyrene or poly(2-substituted methyl acrylates) with molecular weights of 19 800 or greater and for branched structures (polystyrene stars and combs) for which the branch lengths were substantial (100 or more monomer units). Further, the value of

$$[\eta']_\infty = \lim_{c \to 0} \frac{\eta'_\infty - \eta_s}{\eta_s c} \qquad (1)$$

(solution concentration c in grams/milliliter) is sensitive to the specific side groups on the chain; for example, Table I lists values of $[\eta']_\infty$ for polystyrene, poly(α-methylstyrene), poly(methyl-2-*n*-butyl acrylate), poly(methyl-2-ethyl acrylate), poly(methyl-2-phenyl acrylate), and poly(methyl methacrylate). $[\eta']_\infty$ may reflect the degree to which large side groups are held normal to the main chain backbone direction and their motional freedom restricted rather than simply the size of a given side group or chain. In addition, η'_∞/η_s is independent of solvent viscosity, indicating that the solvent plays an important role in whatever process is responsible for η'_∞ and that time–temperature superposition can be employed; plots of log (η'_∞/η_s) vs. concentration are straight lines over the range of concentrations studied.[4]

Finite concentration viscoelastic data and properties ob-

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