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Compositional Variation of Glass-Transition Temperatures. 7. Copolymers

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ABSTRACT: A thermodynamic theory for the compositional variation of glass-transition temperatures is generalized to include copolymers, providing an equation with no adjustable parameters. Properties required for this relation are glass-transition temperatures and glass-transition increments of heat capacity for the two associated homopolymers and the fully alternating copolymer, and the monomer reactivity ratios. Formal conditions are obtained for the occurrence, nature, and values of absolute extrema in copolymer glass-transition temperatures and glass-transition increments of heat capacity. Previous expressions for the composition dependence of copolymer glass-transition temperatures are derived as secondary approximations to a central equation.

Introduction

The aims of this series of papers are to provide a general theoretical method for the calculation of glass-transition temperatures of single-phase multicomponent systems from pure-component properties, to test this method for a variety of solutions, and to clarify the basis of previous formal prescriptions for the compositional variation of T_g. To serve the purpose of generality while providing expressions for the phenomenon with no adjustable parameters, a thermodynamic approach based on the solution entropy has been adopted.[1-6] The phenomenology of the glass transition and the approximation of single-phase glass-forming mixtures as random solutions give predictive expressions for both their glass-transition temperatures and the associated transition increments of heat capacity. This random-mixing model does not require either the excess enthalpy or excess volume of mixing to be zero;[7] consequently relations for the compositional variation of T_g based on this approximation are more general than those derived on the basis of an ideal solution or athermal solution model. A classical thermodynamic approach was adopted in preference to a description based on a hypothesis of the molecular mechanism of the glass transition for practical reasons—the former has the advantage of incorporating the phenomenological features of the transition while avoiding problems associated with as-yet-unsettled aspects of the detailed nature of vitrification.

In earlier papers of this series the thermodynamic theory has been developed and tested for the isobaric glass transition in miscible blends of polymers,[1,2,8] for the effect of degree of polymerization on homopolymer glass-transition temperatures,[3,4,6] and for the combined variation of blend T_g with the relative amount and molecular mass of homopolymer components.[5] Others[9,10] have also applied the principal relation to miscible blends of polymers; in addition, the theory has been shown to account for the compositional variation of T_g in polymer/plasticizer solutions[11,12] and for the plasticizing effect of water in network epoxies,[13] and an approximation to the primary equation has been used to describe the effect of cross-link density on T_g for network polymers.[14] This last successful application of the theory is of particular note as it suggests the possibility of a single formal description of the compositional variation of T_g for both thermoplastics and thermosets.

The inclusion of amorphous copolymers with single glass transitions within the formalism of the theory must allow for the possibility of both a monotonic variation of T_g with composition, as occurs, for example, in styrene–butadiene copolymers,[15] and an absolute extreme value of T_g as a function of composition,[16] such as occurs, for example, in ethyl acrylate–vinylidene chloride copolymers.[17] Any model of copolymers as binary blends of the two constituent mers would, according to the thermodynamic theory, predict a monotonic variation of T_g with composition.[1-6] However, as demonstrated below, a formal description of the effect of copolymer composition on glass-transition temperatures can be developed from the thermodynamic theory. This description, which contains no adjustable parameters, constitutes a generalization of the theory to include the possibility of compound formation.

Theory

Mer–mer interactions in single-phase copolymers can, if those for like and unlike mers are similar in nature and intensity, give rise to glass-transition properties close to those of a miscible blend of the two corresponding homopolymers. On the other hand, if the interactions of like and unlike mers differ significantly, the copolymer is a quasi-binary system. In the nearest-neighbor approximation the copolymer is, in effect, a miscible blend of like and unlike dyads, all three components with characteristic and, in general, different glass-transition properties. Consistent with this notion, the three components are the two homopolymers and the alternating copolymer. The presumed dominance of nearest-neighbor interactions then establishes the copolymer glass-transition behavior as that of a random solution of the three kinds of mer pairs. Denoting dyad fractions for the two homopolymers and the alternating copolymer by, in turn, f_{ii}, f_{jj}, and f_{ij} and using subscripts in this manner to distinguish homopolymer and alternating copolymer glass-transition temperatures and glass-transition increments of heat capacity (these increments approximated as temperature independent[18]), we write the thermodynamic relation for the copolymer glass-transition temperature, in the absence of end effects, as

$$\ln T_g = [f_{ii}\Delta C_{p_{ii}} \ln T_{g_{ii}} + f_{ij}\Delta C_{p_{ij}} \ln T_{g_{ij}} + f_{jj}\Delta C_{p_{jj}} \ln T_{g_{jj}}]/[f_{ii}\Delta C_{p_{ii}} + f_{ij}\Delta C_{p_{ij}} + f_{jj}\Delta C_{p_{jj}}] \quad (1)$$

The denominator of eq 1 is the glass-transition increment of heat capacity[5] per copolymer dyad, ΔC_p.

As the copolymer is a quasi-binary solution, f_{ii}, f_{ij}, and f_{jj} are not independent. Provided the copolymerization equation is applicable, these fractions can be written in terms of the monomer reactivity ratios r_i and r_j and the fraction f_i of i monomers in the copolymer feed ratio[19] to give an alternative form of eq 1

$$\ln T_g = [r_i f_i^2 \Delta C_{p_{ii}} \ln T_{g_{ii}} + 2f_i(1 - f_i)\Delta C_{p_{ij}} \ln T_{g_{ij}} + r_j(1 - f_i)^2 \Delta C_{p_{jj}} \ln T_{g_{jj}}]/[r_i f_i^2 \Delta C_{p_{ii}} + 2f_i(1 - f_i)\Delta C_{p_{ij}} + r_j(1 - f_i)^2 \Delta C_{p_{jj}}] \quad (2)$$

The glass-transition increment of heat capacity for the copolymer is

$$\Delta C_p = [r_i f_i^2 \Delta C_{p_{ii}} + 2f_i(1 - f_i)\Delta C_{p_{ij}} + r_j(1 - f_i)^2 \Delta C_{p_{jj}}]/[r_i f_i^2 + 2f_i(1 - f_i) + r_j(1 - f_i)^2] \quad (3)$$

Formal solutions for values of feed composition at which extrema in T_g occur are obtained from the derivative $\mathrm{d} \ln T_g/\mathrm{d}f_i = 0$ as the roots of

$$(\Delta C_{p_{ii}}\Delta C_{p_{jj}} \ln T_{g_{ii}}/T_{g_{jj}})r_i r_j f_i(1 - f_i) + (\Delta C_{p_{ii}}\Delta C_{p_{ij}} \ln T_{g_{ii}}/T_{g_{ij}})r_i f_i^2 - (\Delta C_{p_{ij}}\Delta C_{p_{jj}} \ln T_{g_{jj}}/T_{g_{ij}})r_j(1 - f_i)^2 = 0 \quad (4)$$

or of the equivalent relation

$$f_i^2[-(\Delta C_{p_{ii}}\Delta C_{p_{jj}} \ln T_{g_{ii}}/T_{g_{jj}})r_i r_j + (\Delta C_{p_{ii}}\Delta C_{p_{ij}} \ln T_{g_{ii}}/T_{g_{ij}})r_i - (\Delta C_{p_{ij}}\Delta C_{p_{jj}} \ln T_{g_{jj}}/T_{g_{ij}})r_j] + f_i[(\Delta C_{p_{ii}}\Delta C_{p_{jj}} \ln T_{g_{ii}}/T_{g_{jj}})r_i r_j + 2(\Delta C_{p_{ij}}\Delta C_{p_{jj}} \ln T_{g_{jj}}/T_{g_{ij}})r_j] - (\Delta C_{p_{ij}}\Delta C_{p_{jj}} \ln T_{g_{jj}}/T_{g_{ij}})r_j = 0 \quad (5)$$

Allowed values of f_i lie between zero and unity. Copolymers for which the homopolymer and alternating copolymer glass-transition properties and monomer reactivity ratios give no physically acceptable solution of eq 4 or 5 have glass-transition temperatures monotonic in f_i. Extreme values of T_g are calculated by substitution in eq 2 of feed composition values, f_i^*, obtained from eq 4 or 5. The solutions of eq 5 are, in general, nondegenerate and, although the eight properties determining these makes difficult a definitive statement, numerical estimates indicate that typically no more than one solution is acceptable. The nature of any compositional extremum in T_g is determined by the sign of the second derivative

$$\left.\frac{\mathrm{d}^2 \ln T_g}{\mathrm{d}f_i^2}\right|_{f_i=f_i^*} \sim (\Delta C_{p_{ii}}\Delta C_{p_{jj}} \ln T_{g_{ii}}/T_{g_{jj}})r_i r_j(1 - 2f_i^*) + 2(\Delta C_{p_{ii}}\Delta C_{p_{ij}} \ln T_{g_{ii}}/T_{g_{ij}})r_i f_i^* + 2(\Delta C_{p_{ij}}\Delta C_{p_{jj}} \ln T_{g_{jj}}/T_{g_{ij}})r_j(1 - f_i^*) \quad (6)$$

The copolymer glass-transition increment of heat capacity can also attain absolute extreme values. From eq 3 the formal values of feed composition, f_i^{**}, at which these occur are the solutions of

$$f_i^2[r_i(\Delta C_{p_{ii}} - \Delta C_{p_{ij}}) + r_j(\Delta C_{p_{ij}} - \Delta C_{p_{jj}}) - r_i r_j(\Delta C_{p_{ii}} - \Delta C_{p_{jj}})] + f_i[r_i r_j(\Delta C_{p_{ii}} - \Delta C_{p_{jj}}) - 2r_j(\Delta C_{p_{ij}} - \Delta C_{p_{jj}})] + r_j(\Delta C_{p_{ij}} - \Delta C_{p_{jj}}) = 0 \quad (7)$$

Again, only for dyad glass-transition properties and monomer reactivity ratios that give physically acceptable values of f_i^{**} can this kind of behavior occur. Analogous to eq 6, the derivative

$$\left.\frac{\mathrm{d}^2 \Delta C_p}{\mathrm{d}f_i^2}\right|_{f_i=f_i^{**}} \sim (\Delta C_{p_{ii}} - \Delta C_{p_{jj}})r_i r_j(1 - 2f_i^{**}) + (\Delta C_{p_{ii}} - \Delta C_{p_{ij}})2r_i f_i^{**} + (\Delta C_{p_{jj}} - \Delta C_{p_{ij}})2r_j(1 - f_i^{**}) \quad (8)$$

determines the nature of any compositional extremum in ΔC_p. Equations 5 and 7 demonstrate that, in general, extrema in T_g and ΔC_p occur at different compositions. As polymers with high glass-transition temperatures usually have low transition increments of heat capacity and vice versa,[20] a maximum in T_g would then be associated with the occurrence of a minimum in ΔC_p and a minimum in T_g with a maximum in ΔC_p.

The maximum fraction of unlike dyads occurs at a feed composition of

$$f_i^+ = 1/[1 + (r_i/r_j)^{1/2}] \quad (9)$$

and is

$$f_{ij}^+ = 1/[1 + (r_i r_j)^{1/2}] \quad (10)$$

As a comparison of eq 5, 7, and 9 illustrates, f_{ij}^+ does not usually coincide with extreme values of T_g nor with extreme values of ΔC_p. Although explicit equations for extreme values of T_g and ΔC_p are somewhat cumbersome, at the maximum fraction of ij dyads simple expressions can be obtained for the copolymer glass-transition temperature and heat capacity increment, respectively T_g^+ and ΔC_p^+. From eq 9 and, in turn, eq 2 and 3

$$\ln T_g^+ = [\Delta C_{p_{ii}} \ln T_{g_{ii}} + 2(r_i r_j)^{-1/2}\Delta C_{p_{ij}} \ln T_{g_{ij}} + \Delta C_{p_{jj}} \ln T_{g_{jj}}]/[\Delta C_{p_{ii}} + 2(r_i r_j)^{-1/2}\Delta C_{p_{ij}} + \Delta C_{p_{jj}}] \quad (11)$$

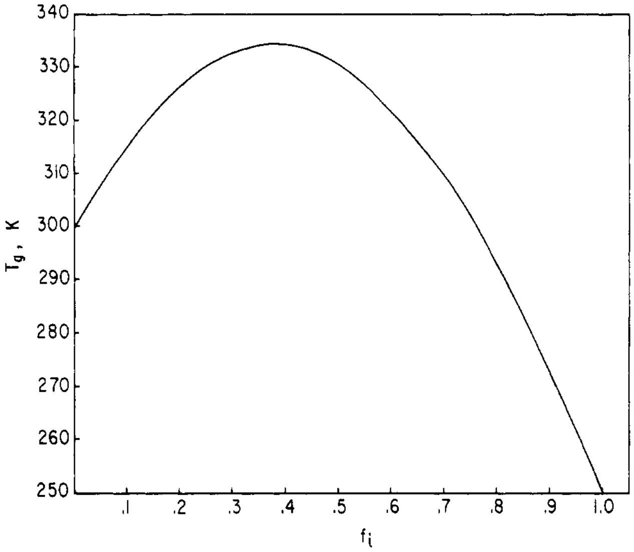

Figure 1. Copolymer glass-transition temperatures as a function of feed composition. For this model calculation $T_{g_{ii}} = 250$ K, $T_{g_{jj}} = 300$ K, $T_{g_{ij}} = 400$ K, and (for convenience) $\Delta C_{p_{ii}} = \Delta C_{p_{jj}} = \Delta C_{p_{ij}}$, $r_i = r_j = 1$.

and

$$\Delta C_p^+ = [\Delta C_{p_{ii}} + 2(r_ir_j)^{-1/2}\Delta C_{p_{ij}} + \Delta C_{p_{jj}}]/2[1 + (r_ir_j)^{-1/2}] \qquad (12)$$

Not unexpectedly, the dependence of copolymer glass-transition temperatures on f_{ij} differs from the dependence of T_g on feed composition. A formal demonstration of this point is afforded by writing

$$\frac{\mathrm{d} \ln T_g}{\mathrm{d}f_{ij}} = \frac{\mathrm{d} \ln T_g}{\mathrm{d}f_i}\frac{\mathrm{d}f_i}{\mathrm{d}f_{ij}} \qquad (13)$$

In the general case, when $\ln T_g$ passes through an extremum and f_{ij} attains a separate maximum, the derivative $\mathrm{d} \ln T_g/\mathrm{d}f_{ij}$ passes through both zero and infinity. The relation between T_g, f_i, and f_{ij} is illustrated in Figures 1 and 2 by the results of a model calculation.

For certain categories of copolymerization, the formalism for extreme values of T_g and ΔC_p simplifies somewhat: examples of these are[21] ideal azeotropic copolymerization ($r_i = r_j = 1$), ideal nonazeotropic copolymerization ($r_i \neq 1$, $r_ir_j = 1$) and greatly preferred addition of both monomers to i monomer ($r_i \gg 1$, $r_j \ll 1$). In the case of greatly preferred addition to i monomers, except at low values of f_i glass-transition properties of the homopolymer formed from j monomers contribute negligibly to copolymer properties.

The analysis is particularly straightforward when the difference between $T_{g_{ii}}$ and $T_{g_{jj}}$ is small compared to the difference between these and $T_{g_{ij}}$ and, similarly, $\Delta C_{p_{ii}} \approx \Delta C_{p_{jj}}$. Formal solutions for f_i^* are then determined solely by the reactivity ratios. Certain combinations of dyad glass-transition properties and monomer reactivity ratios provide a final nontrivial reduction of the theory. For example, an ideal azeotropic copolymerization for the situation outlined above gives

$$f_i^* = f_i^{**} = f_i^+ = f_{ij}^+ = \tfrac{1}{2} \qquad (14)$$

and

$$\ln T_g = \ln T_g^+ = \frac{\Delta C_{p_{ii}} \ln T_{g_{ii}} + \Delta C_{p_{ij}} \ln T_{g_{ij}}}{\Delta C_{p_{ii}} + \Delta C_{p_{ij}}} \qquad (15)$$

If the difference between $\Delta C_{p_{ii}}$ and $\Delta C_{p_{ij}}$ is considered a secondary effect, then eq 15 becomes

$$T_g^* = T_g^+ = (T_{g_{ii}}T_{g_{ij}})^{1/2} \qquad (16)$$

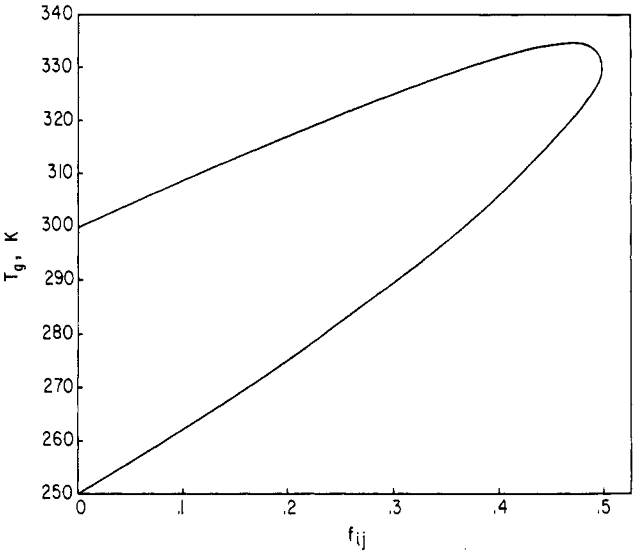

Figure 2. Copolymer glass-transition temperatures as a function of the fraction of unlike dyads. Data for this model calculation as for Figure 1.

Under these conditions T_g^* is a maximum for $T_{g_{ij}} > T_{g_{ii}}$ and a minimum for $T_{g_{ij}} < T_{g_{ii}}$.

First- and Second-Order Forms of Eq 2

The principal relation for T_g recast in the form

$$r_if_i^2\Delta C_{p_{ii}} \ln T_g/T_{g_{ii}} + 2f_i(1 - f_i)\Delta C_{p_{ij}} \ln T_g/T_{g_{ij}} + r_j(1 - f_i)^2\Delta C_{p_{jj}} \ln T_g/T_{g_{jj}} = 0 \qquad (17)$$

and an expansion of the form $\ln (1 + x) \approx x$ gives

$$T_g = [r_if_i^2\Delta C_{p_{ii}} + 2f_i(1 - f_i)\Delta C_{p_{ij}} + r_j(1 - f_i)^2\Delta C_{p_{jj}}]/\left[r_if_i^2\Delta C_{p_{ii}}T_{g_{ii}}^{-1} + 2f_i(1 - f_i)\Delta C_{p_{ij}}T_{g_{ij}}^{-1} + r_j(1 - f_i)^2\Delta C_{p_{jj}}T_{g_{jj}}^{-1}\right] \qquad (18)$$

A different linearized form of eq 2 is obtained by uniform use of the variable T_g as denominator in eq 17. Use of a single-term expansion of the ln terms leads to the expression

$$T_g = [r_if_i^2\Delta C_{p_{ii}}T_{g_{ii}} + 2f_i(1 - f_i)\Delta C_{p_{ij}}T_{g_{ij}} + r_j(1 - f_i)^2\Delta C_{p_{jj}}T_{g_{jj}}]/[r_if_i^2\Delta C_{p_{ii}} + 2f_i(1 - f_i)\Delta C_{p_{ij}} + r_j(1 - f_i)^2\Delta C_{p_{jj}}] \qquad (19)$$

Equation 19, unlike eq 18, is a direct consequence of a model of copolymers as athermal quasi-binary solutions and is therefore the less preferable of the two.

Secondary versions of eq 2 arise from the neglect of the variation of glass-transition increments of heat capacity with dyad composition in eq 18 and 19. These approximations are, respectively,

$$T_g^{-1} = r_if_i^2T_{g_{ii}}^{-1} + 2f_i(1 - f_i)T_{g_{ij}}^{-1} + r_j(1 - f_i)^2T_{g_{jj}}^{-1} \qquad (20)$$

and

$$T_g = r_if_i^2T_{g_{ii}} + 2f_i(1 - f_i)T_{g_{ij}} + r_j(1 - f_i)^2T_{g_{jj}} \qquad (21)$$

Equation 20 is a Fox-type[22] relation for copolymers as single-phase quasi-binary solutions.[16,17] Equation 21 can be obtained[23] from the Gibbs–DiMarzio theory for the glass transition.[24] As eq 18 is a less restricted first-order version of eq 2 than eq 19, the Fox-type expression should be more acceptable than eq 21.

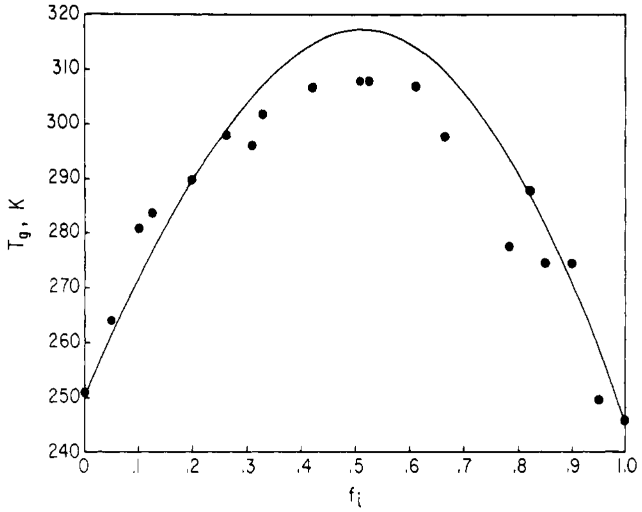

Figure 3. Predicted and observed glass-transition temperatures for copolymers of ethyl acrylate and vinylidene chloride as a function of mole fraction of ethyl acrylate in the copolymer feed. The full line is calculated from eq 22 (i.e., eq 2 with $\Delta C_{p_{ii}} = \Delta C_{p_{ij}} = \Delta C_{p_{jj}}$). Experimental glass-transition temperatures are shown as filled circles.

An additional form of eq 2 arises if only the effect of dyad composition on transition increments of heat capacity is discarded and is

$$\ln T_g = [r_i f_i^2 \ln T_{g_{ii}} + 2f_i(1 - f_i) \ln T_{g_{ij}} + r_j(1 - f_i)^2 \ln T_{g_{jj}}]/[r_i f_i^2 + 2f_i(1 - f_i) + r_j(1 - f_i)^2] \quad (22)$$

The position of this relation in the hierarchy of preferred approximations is, physically, close to that of eq 18.

Comparison of Theory with Experiment

For the ethyl acrylate–vinylidene chloride system the copolymer glass-transition temperature passes through a maximum value of 308 K[17] (at $f_i \approx {}^1/_2$), some 50 K higher than the glass-transition temperature of both poly(ethyl acrylate) ($T_{g_{ii}} = 246$ K)[25] and poly(vinylidene chloride) ($T_{g_{jj}} = 251$ K).[17] Moreover, the monomer reactivity ratios have been calculated ($r_i = 0.95$, $r_j = 1.11$) and the glass-transition temperature for the copolymer prepared in the presence of zinc chloride has been measured[17] ($T_{g_{ij}} \simeq 408$ K). In the absence of information on the relative values of $\Delta C_{p_{ii}}$, $\Delta C_{p_{ij}}$, and $\Delta C_{p_{jj}}$ these were approximated as equal.

Calculated and observed copolymer glass-transition temperatures are compared in Figure 3. The predicted maximum glass-transition temperature, $T_g{}^* = 317$ K, occurs at $f_i{}^* = 0.51$. The difference between theory and experiment in Figure 3 is consistent in sign with the empirical expectation[20] that as $T_{g_{ij}}$ exceeds both $T_{g_{ii}}$ and $T_{g_{jj}}$, $\Delta C_{p_{ij}}$ should be less than both $\Delta C_{p_{ii}}$ and $\Delta C_{p_{jj}}$.

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