Specific Heat Difference between Liquid and Glass: The Contribution of the Conformational and Torsional Specific Heat of Polymer Main Chains and Side Groups

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ABSTRACT: The potential energy map of a dyad in a polymer chain, known as a function of the rotational angles of the backbone carbon–carbon bonds, is utilized to estimate the contribution of the conformational degrees of freedom to the specific heat change at the glass transition. The expected contribution is calculated first for the case where, in the glass, only the transitions among different rotational isomers are frozen and then for the case where the changes in the polymer conformations including even the torsional oscillations of the mainchain bonds are totally frozen. These calculated specific heats, when combined with the contribution of the frozen free volume in the glass, are still insufficient to explain the observed difference in the specific heat between liquid and glass. The present results confirm the earlier conclusion derived from considerations based on the rotational isomeric states model of polymer chains. More detailed calculations are made for poly(vinyl acetate) and poly(methyl methacrylate) to include the effect of the rotation of the side groups, but they result in a similar conclusion. It is suggested that the observed ΔC_p at T_g may be fully accounted for only by taking into consideration the change in the intermolecular nearest neighbor coordination which is allowed in the liquid but frozen in the glass.

When a polymeric liquid is cooled through its glass-transition temperature T_g, some of the degrees of freedom become progressively sluggish to readjustments and eventually stay frozen while the temperature changes. The heat capacity change observed at T_g reflects that part of the liquid heat capacity which is associated with the degrees of freedom which become frozen in the glass. In our quest to identify the molecular mechanisms for the formation of glasses, we often attempt to divide the observed heat capacity change ΔC_p into components. Success in this approach is attained when we can account for the total magnitude of ΔC_p by the sum of separate contributions each associated with one of the degrees of freedom postulated to be frozen in the glass.

Two contributions to ΔC_p, which have been mentioned by many, are those associated with freezing-in at T_g of the free volume and the polymer chain backbone conformation. The component of the heat capacity change arising from the frozen-in free volume can be estimated approximately from

$$\Delta C^{\mathrm{fv}} \approx T_g V (\Delta\alpha)^2/\Delta\beta \qquad (1)$$

where V, α, and β are the volume, the thermal expansion coefficient, and the isothermal compressibility, respectively. (The thermodynamic basis of eq 1 is examined in Appendix A.) The conformational component ΔC^{conf} arises because the trans and gauche rotational states of the polymer chain backbone bonds are of different energies, and their relative population changes with temperature in the liquid but not in the glass.

In an earlier publication,[1] we utilized the rotational isomeric states (RIS) model of polymer chains, developed by Flory and co-workers,[2] to calculate ΔC^{conf}. Its value was evaluated there for a series of polymers for which the statistical weight matrices of the bond rotational states are known from other studies. The sum of the two contributions ΔC^{fv} and ΔC^{conf} was, however, found to be much smaller than the observed ΔC_p values for all five polymers considered there in detail.[1] This suggests a need to examine possible contributions to ΔC_p from other sources.

Goldstein[3] made a detailed analysis of the specific heat data obtained by Chang and others[4,5] on several polymeric and nonpolymeric glasses. He found that not all the ΔC_p observed at T_g is attributable to the entropic effect of frozen-in "configuration" which remains constant throughout the glassy region. He asserts that as much as half of the observed ΔC_p arises from effects which change with temperature and suggests contributions from mechanisms such as the changes in the "lattice vibrational frequencies, anharmonicity, and the number of molecular groups participating in secondary relaxations".

There are experimental data suggesting that the vibrational degrees of freedom experience a change at T_g. Koenig and co-workers found that the infrared absorbences of polystyrene[6] (PS), at a number of frequency bands corresponding to both intramolecular and intermolecular vibrations, undergo distinct changes in their temperature coefficients at T_g. Part of these changes undoubtedly occur as a direct result of the change in the volume expansion coefficients at T_g. Hannon and Koenig[7] also observed small but discernible changes in the temperature coefficient of infrared absorbence at the β transition temperature of poly(ethylene terephthalate), a temperature at which no break in the thermal expansion coefficient is normally observable. It appears that not all the observed change in the infrared adsorbence of PS can be attributed to volume change. (Appendix B discusses the possible procedure by which the contribution of the change in the volume expansion coefficient can be allowed for experimentally from the temperature coefficient difference of a physical property observed at T_g.)

Among the contributions to ΔC_p from various vibrational modes, the one due to torsional oscillation of the chain backbone bonds can be estimated readily. If, on lowering the temperature below T_g, only the change in the relative population of conformational isomers is suppressed, but the torsional and other vibrational motions are not affected, then the conformational specific heat ΔC^{conf} evaluated in the previous publication[1] is virtually the only *intramolecular* contribution to ΔC_p. In the RIS model employed, the rotational isomeric states of bonds correspond to statistically weighted mean positions of the bond angles, which in reality can assume a range of values around the mean. If in the glassy state the amplitude of

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Table I

Conformational Specific Heat[a]

	T_g, °C	C_A	C_B	$C_A - C_B$	C_{RIS}
poly(ethylene)	−120	0.148	0.068	0.080	0.057
poly(propylene), iso	−20	0.069	0.049	0.020	0.047
poly(propylene), syndio	−20	0.111	0.092	0.019	0.036
poly(vinyl acetate), iso	30	0.040[b] (0.056)[c] [0.058][b,d]	0.020[b] (0.027)[c] [0.039][b,d]	0.020[b] (0.029)[c] [0.019][b,d]	0.018
poly(vinyl acetate), syndio	30	0.033[b] (0.046)[c] [0.062][b,d]	0.016[b] (0.029)[c] [0.039][b,d]	0.017[b] (0.017)[c] [0.023][b,d]	0.013
poly(vinyl chloride), iso	77	0.078	0.030	0.048	0.016
poly(vinyl chloride), syndio	77	0.072	0.029	0.043	0.040
poly(styrene), iso	100	0.024	0.025	*e*	0.012
poly(styrene), syndio	100	0.033	0.032	*e*	0.013
poly(methyl methacrylate), iso	43	0.028 (0.026)[b] [0.031][b,d]	0.005 (0.011)[b] [0.015][b,d]	0.023 (0.015)[b] [0.016]	0.013
poly(methyl methacrylate), syndio	160	0.025 (0.016)[b] [0.027][b,d]	0.021 (0.013)[b] [0.027][b,d]	0.004 (0.003)[b] [0.0][b,d]	0.015

[a] In units of cal/(g °C). [b] From the energy map of ref 11. [c] From the energy map of ref 10. [d] Side chain rotations and their energies included. [e] Only a single low-energy domain in the conformational energy map.

the torsional oscillation around the mean is also suppressed, the energy associated with the oscillation will be reflected in ΔC_p as an additional contribution. In the extreme limit where the torsional oscillation is completely frozen in the glassy state, all the potential energy associated with the range of rotational bond angles allowed in the liquid state will be contributing to ΔC_p. In this work, we calculate the total *intramolecular* specific heat of polymer chains by averaging the energy over the potential energy map given as a function of backbone bond rotational angles. This will set an upper limit for the intramolecular conformational and torsional contributions to ΔC_p observable at T_g.

Main Chain Conformational Specific Heat

The potential energy maps as a function of the rotational angles ϕ_i and ϕ_{i+1} of two succeeding bonds in the chain backbone have been calculated for a number of polymers by Flory and co-workers[8-13] as a precurser to evaluation of rotational isomeric states. These maps include the intrinsic threefold torsional potential around C–C bonds, nonbonded interactions between atoms which are proximate, and sometimes bond angle deformation energies. We utilize these maps for the present calculations.

The average conformational energy of a pair of bonds (i and $i + 1$) is evaluated by

$$\langle E \rangle = (1/Z) \int \int E \exp(-E/kT)\, d\phi_i\, d\phi_{i+1} \qquad (2)$$

where

$$Z = \int \int \exp(-E/kT)\, d\phi_i\, d\phi_{i+1} \qquad (3)$$

By evaluating $\langle E \rangle$ at $T = T_g + 50$ and T_g and dividing the difference by 50, the intramolecular specific heat C_A is obtained. This includes the effect of the changing relative population of the rotational isomers as well as the change in the extent of torsional oscillation about the backbone bonds. The results, calculated by approximating the integrals in eq 2 and 3 by summation at 20° intervals, are tabulated in the third column of Table I.

The specific heats C_{RIS} previously calculated[1] from the RIS model are listed in the last column of Table I. The difference between C_A and C_{RIS} arises primarily from the torsional oscillation of bonds about the mean rotational angles. In the RIS model, the mean angle and the energy of each rotational isomeric state are usually taken as independent of temperature. The position of the mean rotational angle is fairly insensitive to temperature change. For the calculation of polymer chain dimensions which depend primarily on mean rotational angles, the temperature-independent rotational isomeric states offer a good approximation. For the calculation of specific heats, the contribution arising from the change in the average energy of each isomeric state with temperature may need to be accounted for. This point is examined in detail below, with poly(vinyl acetate) (PVAc) taken as the example.

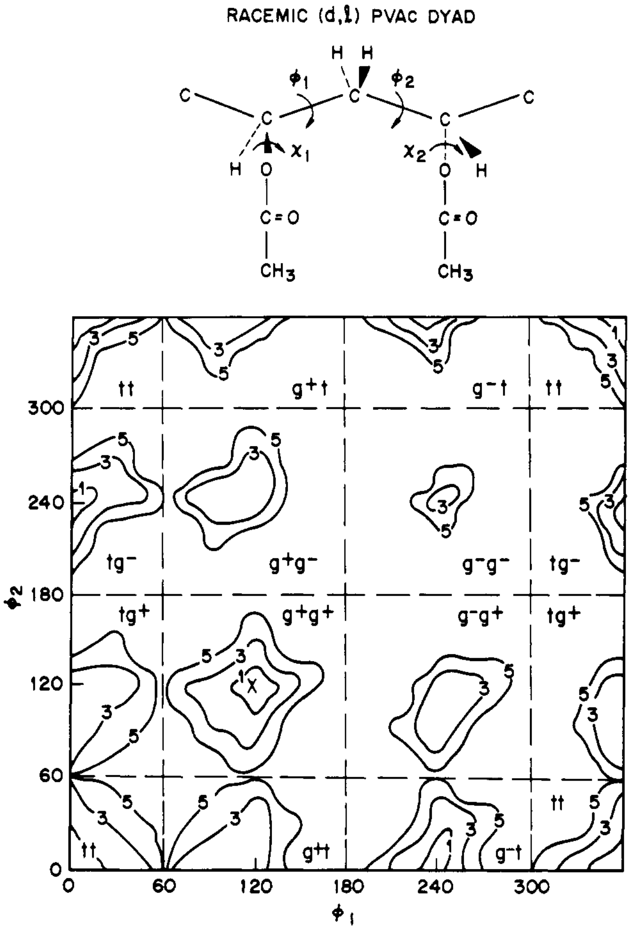

Figure 1. Conformational energy map for a racemic (*d,l*) dyad in PVAc. Energy contours are expressed in kcal/mol of dyad relative to the minimum energy conformation in the g^+g^+ domain denoted with an "X". Each energy corresponds to the most probable (lowest energy) side-chain conformations (χ_1,χ_2).

Figure 1 shows the energy contours calculated by one of us[11] for the racemic (*d,l*) dyad in PVAc. There are nine

Table II
Conformational Characteristics of PVAc Domains (ζ) Calculated[11] for the Syndiotactic Polymer from Figure 1

domain (ζ)	z_ζ 30 °C	α_ζ 30 °C	$\langle e_\zeta \rangle$, cal/g 30 °C	-20 °C	80 °C
tt	0.91	2.21	6.2	5.6	8.8
tg^+	0.26	3.03	17.2	16.6	17.6
tg^-	0.75	1.51	4.9	4.0	6.0
g^+t	0.26	3.03	17.2	16.6	17.6
g^+g^+	1.11	1.59	2.5	1.3	3.9
g^+g^-	0.29	2.58	15.3	14.8	15.8
g^-t	0.75	1.51	4.9	4.0	6.0
g^-g^+	0.29	2.58	15.3	14.8	15.8
g^-g^-	0.03	1.16	25.6	25.6	25.6

energy minima corresponding to various combinations of gauche and trans conformations of the two bonds. Each of these minimum energy states is separated from its neighbors by energy barriers at least 5 kcal/mol. The whole (ϕ_1,ϕ_2) space can therefore be conveniently divided up into domains, as indicated by the broken lines in Figure 1, each surrounding an energy minimum. In each domain ζ, the partition function z_ζ and the average energy $\langle e_\zeta \rangle$ can be calculated by equations similar to eq 2 and 3 but with the integration extending only within the domain boundaries. The values of z_ζ and $\langle e_\zeta \rangle$ and the pre-exponential factor α_ζ defined by

$$z_\zeta = \alpha_\zeta \exp(- \langle e_\zeta \rangle / kT) \tag{4}$$

all evaulated at 30 °C are given in Table II. When the variations in these parameters with temperature are neglected, the specific heat from the change in the population of rotational isomers is given by

$$C_{\mathrm{RIS}} = \frac{\Delta \langle E \rangle}{\Delta T} = \frac{\Delta}{\Delta T}[\{\sum_\zeta \langle \mathrm{e}_\zeta \rangle \alpha_\zeta \exp(- \langle e_\zeta \rangle / kT)\} / \{\sum_\zeta \alpha_\zeta \exp(-\langle e_\zeta \rangle / kT)\}] \tag{5}$$

α_ζ and $\langle e_\zeta \rangle$ being constants. This is essentially what has been done in the previous publication[1] and also for the values of C_{RIS} listed in Table I.

A more exact value of the rotational isomeric specific heat can be obtained by allowing for the temperature dependence of $\langle e_\zeta \rangle$, which in this work was calculated for the temperatures -20 °C (T_g - 50 °C), 30 °C (T_g), and 80 °C (T_g + 50 °C), as shown in Table II. The specific heat C_B, given in the fourth column of Table I, was evaluated by means of the last expression in eq 5 with the value of $\langle e_\zeta \rangle$ appropriate to -20 and 30 °C (T_g) and with the value of α_ζ corresponding to 30 °C. In evaluating C_B, therefore, the relative population of gauche-trans conformers is assumed to remain frozen as the temperature is lowered below T_g.

The physical meaning of the three types of specific heat given in Table I is as follows. If at the onset of the glass transition the torsional oscillation as well as the transitions from one rotational energy minimum to another are completely suppressed, the full magnitude of C_A would be realized as an observable contribution to ΔC_p at T_g. If, on the other hand, the torsional oscillation is fully allowed and only the transition between rotational isomers is prohibited in the glass, then the specific heat of the glass will still retain C_B as the component of specific heat arising from torsional oscillation. The observed ΔC_p will then reflect the change in the conformational specific heat from C_A in the liquid to C_B in the glass. The difference C_A - C_B should be equal to C_{RIS} if the two methods of calculation are exactly equivalent. The results given in Table I show that they are considerably different in many cases. The difference arises partly because of the numerical inaccuracy resulting from replacing the integration by summation at relatively large angular increments. It also arises because the assignments of rotational isomeric states in the two methods are not the same with some polymers. For example, with PS the RIS model assumes four isomeric states, whereas in the present method none of the energy minima in the potential energy map is separated by an energy barrier of 5 kcal/mol or more and therefore only a single isomeric state is assigned to the whole (ϕ_i,ϕ_{i+1}) space. The 5-kcal/mol barriers gave rise to three domains for polypropylene (PP) and five domains for poly(methyl methacrylate) (PMMA), while for the rest of the polymers shown in Table I the number of domains was equal to nine.

Effect of Side Chain Rotation

When the polymer chain has a side group, the conformational energy depends not only on the main-chain rotational angles ϕ_i and ϕ_{i+1} but also, to some extent, on the rotational state of the side group. The energy map, such as that shown in Figure 1, is usually evaluated for the side-chain rotational angles which render the energy a minimum at the given (ϕ_i,ϕ_{i+1}) angles. For more detailed considerations, the appropriate approach would be to construct an energy map as a function of four angles ϕ_i, ϕ_{i+1}, χ_{i-1}, and χ_{i+1}, the latter two denoting the rotational angles of the side chains attached to the carbons (i - 1) and (i + 1). Among the polymers listed in Table I, only PVAc and PMMA merit such detailed consideration. The rotation of the methyl side group in PP is likely[9] to result in negligibly small changes in the energy. In the case of PS, on the other hand, the phenyl group is confined,[12,14,15] by large energy barriers, to such a small angular range that any possible effect of its rotation can be neglected. For PVAc and PMMA the potential energy maps are available to us[11] as a function of the four angles ϕ_i, ϕ_{i+1}, χ_{i-1}, and χ_{i+1}, and therefore the calculation discussed in the previous section was performed for both with the side-chain rotations fully taken into account. Thus for the total intramolecular conformational specific heat C_A of the liquid polymer, the integrations indicated by eq 2 and 3 were performed with respect to the four angles. The numerical results, obtained by approximating the integration by summation at 20° intervals for ϕ_i and ϕ_{i+1} and at 30° intervals for χ_{i-1} and χ_{i+1}, are given in Table I (the figures in square brackets). A similar calculation was also made for the conformational specific heat C_B of the glassy polymer (on the assumption of frozen conformational transitions). Inclusion of the side-chain rotations increases both C_A and C_B by about 0.020 cal/(g °C) for isotactic as well as syndiotactic PVAc[16]. The difference C_A - C_B, however, remains at about 0.020 cal/(g °C), similar to the equivalent C_A - C_B value without the effect of the side-chain rotation specifically taken into account. The same conclusion can be drawn for PMMA. This detailed calculation thus confirms the intuitive deduction that the side-chain rotation is effectively separable from the main-chain motions, and, as long as the side-chain rotation itself is not frozen at the onset of the glass transition, its contribution to ΔC_p can be neglected.

Discussion

Table III summarizes the observed ΔC_p values and the free-volume contribution ΔC^{fv} calculated by eq 1 for the several polymers discussed in the previous paper.[1] The difference ΔC_p - ΔC^{fv} is often considered to arise from the freeze-in of polymer main-chain conformation in the glass. If the torsional oscillations about bonds are fully allowed

Table III
Comparison of Various Contributions to ΔC_p[a]

	ΔC_p (exptl)	ΔC^{fv} (eq 1)	$\Delta C_p - \Delta C^{\mathrm{fv}}$	$C_A - C_B$ (Table I)	C_A (Table I)
poly(vinyl acetate)	0.120	0.041	0.079	0.017-0.029	0.033-0.056 [0.058-0.062][b]
poly(vinyl chloride)	0.068	0.031	0.037	0.043-0.048	0.072-0.078
poly(styrene)	0.071	0.034	0.037		0.023-0.033
poly(methyl methacrylate), atactic	0.070	0.033	0.037	0.004-0.023	0.025-0.028 [0.027-0.031][b]
poly(methyl methacrylate), isotactic	0.111	0.062	0.049	0.015-0.023	0.028 [0.031][b]

[a] All in units of cal/(g °C). [b] Side-chain rotation included.

and only the transition between trans and gauche conformations is prevented in the glass, the heat capacity change at T_g from the conformational effect is expected to be equal to $C_A - C_B$ calculated in the Main Chain Conformational Specific Heat section. As is seen in Table III, the $C_A - C_B$ value, calculated for either of the stereoregular varieties of a given polymer, is much smaller than the experimentally derived values of $\Delta C_p - \Delta C^{\mathrm{fv}}$ for the corresponding atactic polymers, poly(vinyl chloride) (PVC) being the only exception. This reconfirms the conclusion derived in the previous paper[1] on the basis of the RIS model calculations.

If, in the glass, all changes in the main-chain conformations including the torsional oscillations are frozen, the change in C_p at T_g arising from this source will be equal to C_A calculated in the Main Chain Conformational Specific Heat section. But Table III shows that, except for PVC, the full magnitude of C_A is still not enough to account for the experimentally observed value of $\Delta C_p - \Delta C^{\mathrm{fv}}$. It is difficult to estimate the extent to which the torsional oscillation of main-chain bonds is suppressed in the glass. Even a limited distortion of rotational angles of a large number of bonds cannot take place simultaneously without resulting in a gross change of the overall conformation of the molecule. Only a well-coordinated torsional motion of several neighboring bonds can be accomplished without disturbing the rest of the chain conformation. It is therefore likely that a sizable contribution to ΔC_p may arise from the torsional specific heat. Table III, however, shows that the observed ΔC_p contains contributions even larger than the totally frozen torsional oscillations could make. This extra contribution must come from the frozen *intermolecular* configuration.

The specific heat changes discussed in this work have been evaluated from a purely classical approach. The proper treatment of vibrational specific heat has to be quantum mechanical and should include consideration of discrete vibrational energy levels. Such a quantum-mechanical treatment of main-chain torsional oscillation of polymers, based on realistic polymer chain conformations as discussed here, does not seem feasible at present.[20] The classical treatment given here is believed to afford a good approximation in view of the rather weak force constants involved in the torsional oscillations. An indirect support for this also comes from the fact that the rotational isomeric states approximation of polymer chains, which itself is derived from classical treatment of distribution of states over main-chain rotational angles, has enjoyed good agreement with experiment.[2]

The importance of the contribution of vibrational specific heat to the observed ΔC_p has been increasingly recognized. In a recent paper, DiMarzio and Dowell,[21] for example, make use of the Einstein model to estimate the vibrational contribution to ΔC_p arising from the change in the thermal expansion coefficient at T_g. In discussing contributions to ΔC_p, especially of vibrational nature, it is important that two types of effects have to be clearly differentiated. The first of these arises directly from the fact that the thermal expansion coefficient changes at T_g (and hence the stiffness constant of the matrix, within which the vibration occurs, also undergoes a change in its temperature coefficient at T_g). The second effect, of more fundamental importance, arises from the fact that the rate of structure change with temperature in the liquid is different from that in the glass even at the same volume or at the same rate of volume expansion. Appendix B discusses the method of eliminating the first effect from an observed quantity ϕ. By substituting S for ϕ, one can derive

$$\Delta C_V = \Delta C_p - TV\Delta(\alpha^2/\beta) \tag{6}$$

$$\Delta C_{\alpha=\alpha_l} = \Delta C_p - TV(\alpha_g/\beta_g)\Delta\alpha \tag{7}$$

$$\Delta C_{\alpha=\alpha_g} = \Delta C_p - TV(\alpha_l/\beta_l)\Delta\alpha \tag{8}$$

The specific heats at constant volume, ΔC_V, and at constant thermal expansion, $\Delta C_{\alpha=\alpha_l}$ and $\Delta C_{\alpha=\alpha_g}$, are all somewhat larger than the values of $\Delta C_p - \Delta C^{\mathrm{fv}}$ given in Table III. The conformational specific heat calculated in this work is considered, to a good approximation, independent of volume expansion. Thus, irrespective of how we choose to allow for the differing volume expansion between the liquid and the glass, either in terms of the free-volume concept as in Table III or by means of eq 6–8, the *intra*molecular effect alone is far from sufficient to explain the observed specific heat difference between liquid and glass.

On cooling the liquid, the onset of glass transition is probably accompanied by freezing in of not only the free volume and the polymer main-chain conformation but also of the intermolecular neighbor coordination. An atom or segment in a polymer chain is surrounded by 8 to 12 neighbors of which usually only four are connected by covalent bonds. The rest are coordinated through secondary bonding forces, and in the liquid, where the nearest neighbor coordination changes with temperature, the changing interaction with neighbors will be reflected as a contribution to the specific heat. Part of the overall effect of this changing nearest neighbor configuration can undoubtedly be attributed to the change in the average distance between neighbors and hence the change in volume with temperature. It is, however, possible that different nearest neighbor configurations occupying the same average volume may still possess different potential energies and also present different force fields within which vibrations of nearby atomic groupings occur. In the liquid, those configurational states having higher potential and vibrational energies are sampled less and less frequently as the temperature is lowered. At T_g when the free volume freezes in, so does the nearest neighbor coordination configuration, as well as the intramolecular conformation of the main chain. Then the sampling frequency of nearest neighbor configurational states of different energies can no longer change with a further decrease in temperature. In summary, what we propose here is that the full magnitude of the observed ΔC_p at T_g can be accounted for only by noting the process of freezing-in of *inter*molecular as well as the *intra*molecular conformation and configurational states.

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Appendix A

Equation 1 has been used in this work for approximate estimation of the component of the heat capacity change at T_g which arises from freezing-in of free volume. Equation 1 was first derived by Goldstein[17] from a thermodynamic argument and later by Nose[18] on the basis of a specific model of glass-forming liquid. Here we reexamine the derivation of eq 1 and its validity more closely.

We adopt the notations and concepts developed in a previous paper[19] to describe the thermodynamic state of a glass-forming system. Its Gibbs free energy is assumed to be describable as a function of T, p, and a set of ρ order parameters $z_1, z_2, ..., z_\rho$. In the liquid, the order parameters assume the values which minimize the free energy, while in the glass some or all of the order parameters fail to attain the equilibrium values. For convenience, we assume z_1 to represent the free-volume content in the system.

The heat-capacity change at T_g under constant volume ΔC_V can be estimated by the well-known thermodynamic relation

$$\Delta C_V = \Delta C_p - TV\Delta(\alpha^2/\beta) \tag{A1}$$

The inappropriateness of using $\Delta C_p - \Delta C_V$ as a measure of the frozen-in free-volume contribution ΔC^{fv} was pointed out previously,[1] since a temperature change under constant total volume will lead to adjustment of both the free and the occupied volume to seek a new minimum free-energy state. What we need is the heat-capacity change $\Delta C_{V,z_1}$ under the simultaneous constancy of the total volume V and the free volume z_1. However, no equilibrium process which preserves V and z_1 simultaneously can be carried out. The next best thing would be to evaluate the specific heat change ΔC_{z_1} under constant free volume and use $\Delta C_p - \Delta C_{z_1}$ as an approximate measure of the free-volume component, i.e.,

$$\Delta C^{\mathrm{fv}} \approx \Delta C_p - \Delta C_{z_1} \tag{A2}$$

From a point on the (T,p) plane in the liquid state, one can always find a path along which the equilibrium z_1 value remains constant. The liquid heat capacity under constant z_1 can be evaluated from the change in S along this curve:

$$C_{z_1}{}^{l} = T\,(\partial S/\partial T)_{z_1,A=0} \tag{A3}$$

where $\boldsymbol{A} = 0$ signifies that all the affinities $A_1, ..., A_\rho$ remain zero along it. The difference between $C_{z_1}{}^{l}$ and the usual isobaric heat capacity is given by

$$C_p{}^{l} - C_{z_1}{}^{l} = TV\alpha_l\,(\partial p/\partial T)_{z_1,A=0} \tag{A4}$$

where $(\partial p/\partial T)_{z_1,A=0}$ is the slope of the constant z_1 curve on the liquid (T,p) plane.

By performing similar measurements on a much faster scale, one can obtain properties pertaining to the glassy state. We denote by $C_{z_1}{}^{g}$ the heat capacity obtainable from a fast experiment in which T and p are varied in the direction given by the slope $(\partial p/\partial T)_{z_1,A=0}$. Thus,

$$C_{z_1}{}^{g} = T\,(\partial S/\partial T)_{z_1,\boldsymbol{z}'} \tag{A5}$$

where $\boldsymbol{z}'$ is the set of z_i's which remain frozen in the glassy state. $\boldsymbol{z}'$ may or may not include z_1 depending on whether free volume does or does not in fact remain constant in the glass during the fast experiment being considered. The first subscript z_1 in (A5) signifies that the derivative is evaluated in the direction given by $(\partial p/\partial T)_{z_1,A=0}$ in the equilibrium liquid. The usual heat capacity of a glass is obtained from a fast experiment under constant pressure:

$$C_p{}^{g} = T\,(\partial S/\partial T)_{p,\boldsymbol{z}'} \tag{A6}$$

By analogy to (A4) one can write:

$$C_p{}^{g} - C_{z_1}{}^{g} = TV\alpha_g\,(\partial p/\partial T)_{z_1,A=0} \tag{A7}$$

In view of the importance of (A7) for the present discussion, we give its step-by-step derivation here. For a glass in which all the order parameters belonging to $\boldsymbol{z}'$ are frozen, the Gibbs free energy and the entropy are each a function of two variables T and p only. The derivatives of S along different directions on the (T,p) plane can be related by

$$(\partial S/\partial T)_{p,\boldsymbol{z}'} - (\partial S/\partial T)_{z_1,\boldsymbol{z}'} = -(\partial S/\partial p)_{T,\boldsymbol{z}'}\,(\partial p/\partial T)_{z_1,A=0} \tag{A8}$$

The Maxwell relation holds for a glass:

$$(\partial S/\partial p)_{T,\boldsymbol{z}'} = -(\partial V/\partial T)_{p,\boldsymbol{z}'} = V\alpha_g \tag{A9}$$

Combining (A8) and (A9) with the definitions of (A5) and (A6) gives relation A7.

Subtraction of (A7) from (A4) leads to

$$\Delta C_p - \Delta C_{z_1} = TV\Delta\alpha\,(\partial p/\partial T)_{z_1,A=0} \tag{A10}$$

In the previous paper,[19] it was shown that

$$(\partial p/\partial T)_{z_1,A=0} = \Delta\alpha/\Delta\beta \tag{A11}$$

if and only if the volume is a function of T, p, and z_1 only:

$$V = V(T,p,z_1) \tag{A12}$$

Combining (A10) and (A11) we have

$$\Delta C_p - \Delta C_{z_1} = TV(\Delta\alpha)^2/\Delta\beta \tag{A13}$$

(A12) is an important restriction for the validity of (A13). It is quite possible that different conformational isomers of the same polymer molecule might occupy different core volumes, and if so V will be a function also of the order parameter denoting the conformer populations.

Equation 1 is only an approximation due to the approximate equality of (A2) and also because of the possible violation of (A12). Whether any relation giving a better approximation than eq 1 can be derived purely on the basis of thermodynamics alone is questionable. The difficulty stems from the fact that a thermodynamic quantity ΔC_p cannot be divided exactly into components unless the contributing factors are all decoupled from each other.

Appendix B

When a property ϕ, such as the infrared absorbence at a certain frequency band, is measured as a function of temperature, its temperature coefficient may show an abrupt change at T_g. It is then desirable to know how much of this change is the direct result of the concommitant change in thermal expansion coefficient at T_g and how much of it reflects additional structural differences between the liquid and the glass.

We derive here thermodynamic relations with which the observed coefficients $(\partial\phi/\partial T)_p$ for liquid and glass can be reduced to a common volume expansion. This is done in three different ways: (i) evaluate $(\partial\phi/\partial T)_V$ for both liquid and glass and compare them; (ii) evaluate $(\partial\phi/\partial T)^{g}_{\alpha=\alpha_l}$ for a glass which would obtain if the temperature coefficient of ϕ were observed under varying pressure so as to keep the volume expansion of the glass the same as that of the liquid and compare it with $(\partial\phi/\partial T)_p{}^{\mathrm{l}}$ observed for liquid in the normal manner; and (iii) evaluate $(\partial\phi/\partial T)^{\mathrm{l}}{}_{\alpha=\alpha_{\mathrm{g}}}$ for the liquid with volume expansion held the same as in the glass and compare it with the ordinary glass property $(\partial\phi/\partial T)_p{}^{\mathrm{g}}$. (The superscripts l and g are to denote properties pertaining to liquid and glass, respectively, and are used here in place of the subscripts $\boldsymbol{A} = 0$ and $\boldsymbol{z}'$ in Appendix A.)

$(\partial\phi/\partial T)_V$ can be related to $(\partial\phi/\partial T)_p$ through the standard relation effecting the change of variables:

$$(\partial\phi/\partial T)_V{}^{\mathrm{l}} = (\partial\phi/\partial T)_p{}^{\mathrm{l}} + (\partial\phi/\partial p)_T{}^{\mathrm{l}}\,(\partial p/\partial T)_V{}^{\mathrm{l}} = (\partial\phi/\partial T)_p{}^{\mathrm{l}} + (\partial\phi/\partial p)_T{}^{\mathrm{l}}(\alpha_{\mathrm{l}}/\beta_{\mathrm{l}}) \tag{B1}$$

By taking the difference of (B1) from the similar expression pertaining to the glass we have:

$$\Delta(\partial\phi/\partial T)_V = \Delta(\partial\phi/\partial T)_p + \Delta[(\partial\phi/\partial p)_T(\alpha/\beta)] \tag{B2}$$

$(\partial\phi/\partial T)^{\mathrm{g}}{}_{\alpha=\alpha_{\mathrm{l}}}$, which one would obtain by performing a fast measurement by changing both T and p simultaneously so as to maintain its thermal expansion to correspond to α_{l}, is given by:

$$(\partial\phi/\partial T)^{\mathrm{g}}{}_{\alpha=\alpha_{\mathrm{l}}} = (\partial\phi/\partial T)_{\mathrm{p}}{}^{\mathrm{g}} + (\partial\phi/\partial V)_T{}^{\mathrm{g}}\,[(\partial V/\partial T)_p{}^{\mathrm{l}} - (\partial V/\partial T)_p{}^{\mathrm{g}}] = (\partial\phi/\partial T)_p{}^{\mathrm{g}} - (\partial\phi/\partial p)_T{}^{\mathrm{g}}(\Delta\alpha/\beta_{\mathrm{g}}) \tag{B3}$$

By substracting (B3) from $(\partial\phi/\partial T)^{\mathrm{l}}{}_{\alpha=\alpha_{\mathrm{l}}} = (\partial\phi/\partial T)_p{}^{\mathrm{l}}$, we obtain:

$$\Delta(\partial\phi/\partial T)_{\alpha=\alpha_{\mathrm{l}}} = \Delta(\partial\phi/\partial T)_p + (\partial\phi/\partial p)_T{}^{\mathrm{g}}(\Delta\alpha/\beta_{\mathrm{g}}) \tag{B4}$$

One may also perform a slow measurement in which T and p are altered to maintain the volume expansion equal to α_{g}. $(\partial\phi/\partial T)^{\mathrm{l}}{}_{\alpha=\alpha_{\mathrm{g}}}$ thus determined would be related to $(\partial\phi/\partial T)_p{}^{\mathrm{l}}$ by:

$$(\partial\phi/\partial T)^{\mathrm{l}}{}_{\alpha=\alpha_{\mathrm{g}}} = (\partial\phi/\partial T)_p{}^{\mathrm{l}} - (\partial\phi/\partial V)_T{}^{\mathrm{l}}\,[(\partial V/\partial T)_p{}^{\mathrm{l}} - (\partial V/\partial T)_p{}^{\mathrm{g}}] = (\partial\phi/\partial T)_p{}^{\mathrm{l}} + (\partial\phi/\partial V)_T{}^{\mathrm{l}}(\Delta\alpha/\beta_{\mathrm{l}}) \tag{B5}$$

Subtraction of $(\partial\phi/\partial T)^{\mathrm{g}}{}_{\alpha=\alpha_{\mathrm{g}}} = (\partial\phi/\partial T)_{\mathrm{p}}{}^{\mathrm{g}}$ from (B5) leads to:

$$\Delta(\partial\phi/\partial T)_{\alpha=\alpha_{\mathrm{g}}} = \Delta(\partial\phi/\partial T)_p + (\partial\phi/\partial p)_T{}^{\mathrm{l}}(\Delta\alpha/\beta_{\mathrm{l}}) \tag{B6}$$

The expressions B2, B4, and B6 give the methods of correcting the observed difference in the temperature coefficients of ϕ in the liquid and the glass to allow for their different volume expansions. To utilize these, one has to have additional data on the pressure coefficient of ϕ for the liquid, for the glass, or for both.

The correction term, or the last term on the right of each of expressions B2, B4, and B6, becomes the same if:

$$(\partial\phi/\partial p)_T{}^{\mathrm{g}}/\beta_{\mathrm{g}} = (\partial\phi/\partial p)_T{}^{\mathrm{l}}/\beta_{\mathrm{l}} \tag{B7}$$

or

$$(\partial\phi/\partial V)_T{}^{\mathrm{g}} = (\partial\phi/\partial V)_T{}^{\mathrm{l}} \tag{B8}$$

Thus, to the approximation that the dependence of the property ϕ on the volume can be considered the same for glass and for liquid, the three expressions B2, B4, and B6 can be used interchangeably.

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Effect of Nonrandomness in Polymer-Solution Thermodynamics

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ABSTRACT: Polymer solutions are described by a modified form of Flory's partition function which provides an approximate, but satisfactory, representation of liquid binary mixtures at low pressures. The random-mixing assumption is rejected; to take nonrandomness into account, a two-fluid theory is used, coupled with the local composition concept. Theoretical expressions are derived for free energy, enthalpy, entropy, chemical potential, and other partial molar quantities. Characteristic parameters for pure components are evaluated according to usual methods, because Flory's model remains unchanged when applied to pure liquids. The properties of four polymer–solvent systems are interpreted according to the new nonrandom theory. Using only two adjustable parameters, the nonrandom model represents both activity and enthalpies-of-mixing data. For two systems with the same binary parameters, it is also possible to describe volumetric properties at low pressures.

Recently Renuncio and Prausnitz[1] suggested that a limitation of Flory's equation of state extended to mixtures can be ascribed, in part, to the random-mixing assumption. Therefore, they have proposed a phenomenological

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