Contribution of the Conformational Specific Heat of Polymer Chains to the Specific Heat Difference between Liquid and Glass

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ABSTRACT: The abrupt change in C_p at the glass-transition temperature arises from several different contributions. The effect of the frozen-in free volume in the glass can be allowed for approximately through thermodynamic relations, and it is frequently assumed that the remainder arises mostly from the effect of polymer chain conformations frozen-in in the glass. In order to test this hypothesis the conformational specific heat has been calculated by means of the rotational isomeric states model for a number of polymers for each of which the statistical weight matrix was previously established. The result shows that the conformational specific heat comprises only a modest part of the total ΔC_p. It therefore suggests that the glass transition is accompanied by additional effects such as the changes in the vibrational frequencies or in other modes of thermal excitation.

I. Introduction

As the temperature of a supercooled polymeric liquid is lowered toward the glass transition temperature T_g, the relaxation time for structural reorganization increases rapidly until at T_g it becomes much longer than the time scale of experiment. Such an increase in the relaxation time can be noted through observation of many different properties: volume, enthalpy, diffusion coefficient, dynamic shear modulus, etc. Below T_g some of the mechanisms of structural reorganization are obviously forbidden. It is, however, not easy to indicate in molecular terms what are in fact the structural features frozen in the glass.

Traditionally, it has been assumed that the free volume in glasses remains constant. It is often further assumed that the glass transition occurs when the free volume fraction decreases to a certain minimum value. There are, however, many experimental observations which cannot be explained in detail by such a simple free volume concept alone. A few such examples are discussed below.

The properties of a glassy material depend on the past history imposed on the sample. When a glass sample, prepared by quenching from the liquid state, is annealed isothermally at temperatures moderately below T_g, its volume[2a] and heat content[2b] can readily be observed to decrease toward their equilibrium values. A densified glass can also be prepared by applying pressure to the polymeric liquid, lowering the temperature to below T_g, and then relieving the pressure. Two densified samples, one prepared by annealing and the other by pressure cooling, may have the same specific volume and hence the same free volume, and yet exhibit differences in other properties. Whereas the volume decrease on annealing is accompanied by a similar decrease in enthalpy, the pressure-densified glasses show enthalpy values[3-7] which are the same as or even higher than that of a quenched glass. The embrittlement of glassy polymers which accompanies annealing[8] is not observed[9,10] with pressure-densified glasses.

Even the structural relaxation occurring on annealing the glass cannot be described by means of the free volume concept alone. When the relaxations in the volume and the enthalpy were observed[11] with poly(vinyl chloride) annealed under identical conditions, the rates of decrease in the two properties were not found to be proportional to each other. Similarly, the rates of relaxation in the refractive index and the enthalpy of an annealed B_2O_3 glass were observed[12] to deviate from each other. Knowing the volume or the free volume does not thus automatically give information on the degree of relaxation of other properties.

In the discussion of the nonequilibrium thermodynamics of glassy materials, the concept of order parameters has frequently been made use of.[13-17] Order parameters are parameters representing certain structural aspects of the material and are considered the independent variables, in addition to the usual T and p, which are needed to specify the (nonequilibrium) thermodynamic state of a given glass sample. In the traditional view the glass structure is regarded as determined solely by the free volume fraction frozen in during the glass formation, and one can then take the free volume as the only order parameter required for thermodynamic description of a glass. If only a single-order parameter is frozen in at T_g, as is assumed in the simple free-volume theory, the dependence of T_g on pressure can be given by:

$$\mathrm{d}T_g/\mathrm{d}p = T_g V \Delta\alpha/\Delta C_p \tag{I.1}$$

and

$$\mathrm{d}T_g/\mathrm{d}p = \Delta\beta/\Delta\alpha \tag{I.2}$$

where Δ denotes the difference between the properties of the liquid and the glass, and α, β, and C_p refer to the thermal expansion coefficient, isothermal compressibility, and isobaric specific heat. The agreement[4,6,7,14,15,19-28] between eq I.1 and I.2 and experimental data is, however, only marginal, indicating the inadequacy of assuming only a single-order parameter, hence a single structural feature, to be frozen in at T_g.

The examples cited above clearly indicate the need[11,18] for a second-order parameter or a second structural element which becomes immobilized in polymeric glasses. Suggestions[3,5,6,24] have indeed been made previously that the change in the average conformation of polymer chains with temperature has to be taken into account in order to explain the enthalpy of pressure-densified glasses. Since the various rotational states of the bonds in the polymer chain are not of the same energy, the average conformation changes with temperature in the liquid state. As the pressure is applied to the liquid the glass transition occurs at higher temperatures and the resulting densified glass has frozen-in conformations of higher energy.

In recent years the rotational isomeric states (RIS) model of polymer chains has been applied successfully[29] to predict various conformation-dependent properties of polymer molecules in solution and in bulk liquid. Using the numerical values of the parameters in the statistical weight matrices evaluated for many polymers in these applications, we can calculate the contribution of the conformational change to the

0024-9297/78/2211-0114$01.00/0

specific heat of equilibrium liquids. The conformational change is largely suppressed below T_g, and the specific heat difference observed between the liquid and glass at T_g includes the contribution of such conformational specific heat. The purpose of this work is to calculate the conformational specific heat of various polymers using the RIS model and compare it with experimental values of ΔC_p, thereby assessing the importance of the polymer conformation as an order parameter describing the glassy state.

II. Conformational Specific Heat

From the conformational partition function Q summed over all the rotational isomeric states of a polymer chain, the equilibrium conformational energy can be obtained:

$$E_{\mathrm{conf}} = kT^2 \, \mathrm{d} \ln Q/\mathrm{d}T \qquad \text{(II.1)}$$

The partition function Q for a polymer chain of n bonds is evaluated by[29]

$$Q = J^* \left[\prod_{i=2}^{n-1} U_i \right] J \qquad \text{(II.2)}$$

$$J^* = [100 \ldots 0](1 \times \nu); \quad J = \begin{bmatrix} 1 \\ 1 \\ \vdots \\ 1 \end{bmatrix} (\nu \times 1) \qquad \text{(II.3)}$$

where the $\nu \times \nu$ (ν rotational states, usually equal to 3, being assumed about each backbone bond) statistical weight matrix for bond i

$$\begin{array}{cc} \phi_{i-1} & \overline{\quad\quad\phi_i\quad\quad} \\ & \begin{array}{ccc} \alpha & \beta & \gamma \end{array} \\ \mathbf{U}_i = \begin{array}{c} \alpha \\ \beta \\ \gamma \end{array} & \begin{bmatrix} \mu_{\alpha\alpha} & \mu_{\alpha\beta} & \mu_{\alpha\gamma} \\ \mu_{\beta\alpha} & \mu_{\beta\beta} & \mu_{\beta\gamma} \\ \mu_{\gamma\alpha} & \mu_{\gamma\beta} & \mu_{\gamma\gamma} \end{bmatrix} \end{array} \qquad \text{(II.4)}$$

consists of Boltzmann factors $\mu_{\alpha\beta;i} = \exp(-E_{\alpha\beta;i}/RT)$ of the pairwise dependent backbone conformational energies $E_{\alpha\beta;i} = E(\phi_{i-1} = \alpha, \phi_i = \beta)$, ϕ_{i-1} and ϕ_i being the rotational states about backbone bonds $i - 1$ and i.

The values of E_{conf} for a number of polymers, for which fairly reliable values of the parameters of the statistical weight matrices are known (see references in Table I), were evaluated numerically at two temperatures $T = T_g + 50$ °C and $T_g - 50$ °C and from the difference the conformational specific heat at T_g was obtained. The calculated values are summarized in Table I. For several polymers, polystyrene as an example, E_{conf} was calculated over a temperature range wider than $T = T_g \pm 50$ °C. Values of $\mathrm{d}E_{\mathrm{conf}}/\mathrm{d}T$ calculated over the extended temperature range do not deviate significantly from those presented in Table I.

III. Analysis of Specific Heat Data

The specific heats of the liquid and the glass, either measured directly at T_g or extrapolated to T_g from data obtained as a function of temperature, are available for a number of polymers in the literature. The experimentally determined specific heat change at T_g, ΔC_p, can be considered to consist of the following three components:

$$\Delta C_p = \Delta C^{\mathrm{conf}} + \Delta C^{\mathrm{fv}} + \Delta C^{\mathrm{misc}} \qquad \text{(III.1)}$$

If, during the measurement of the glass specific heat, the temperature of the glass is changed more rapidly than the structural relaxation time, the polymer chain conformation and the free volume in the sample presumably remain frozen. The conformation and free volume components, ΔC^{conf} and ΔC^{fv}, in eq III.1 are therefore equal to the conformational and free volume specific heats of the equilibrium liquid at the same temperature. We thus identify ΔC^{conf} with the conformational specific heat of isolated polymer chains calculated from the RIS model in the preceding section.

Table I
Conformational Specific Heat of Polymers Near T_g

Polymer	T_g, °C	$\mathrm{d}E_{\mathrm{conf}}/\mathrm{d}T$, cal/(g °C)
Polydimethylsiloxane[a]	−123	0.032
Polyethylene[a]	−120	0.057
Polypropylene, syndio.[b]	−20	0.036
Polypropylene, iso.[b]	−20	0.047
Poly(*cis*-butadiene)[a]	−108	0.030
Poly(*cis*-isoprene)[a]	−73	0.030
Poly(*trans*-isoprene)[a]	−56	0.009
Polystyrene, syndio.[c]	100	0.012
Polystyrene, iso.[c]	100	0.011
Polystyrene, atactic[c]	100	0.017
Poly(α-methylstyrene), syndio.[d]	192	0.011
Polyoxymethylene[a]	−100	0.081
Poly(1,4-phenylene oxide)[e]	90	0.015–0.028
Poly(2,6-dimethyl-1,4-phenylene oxide)[e]	205	0.017
Poly(2,6-diphenyl-1,4-phenylene oxide)[e]	220	0.007
Poly(2-methyl-6-phenyl-1,4-phenylene oxide)[e]	170	0.014
Poly(methyl methacrylate), syndio.[f]	160	0.015
Poly(methyl methacrylate), atactic[f]	105	0.009
Poly(methyl methacrylate), iso.[f]	43	0.013
Poly(vinyl acetate), syndio.[d]	30	0.013
Poly(vinyl acetate), iso.[d]	30	0.018
Poly(ethylene terephthalate)[a]	69	0.005
Poly(butylene terephthalate)[g]	90	0.014
Polycarbonate[e]	120	0.002
Poly(vinyl chloride), syndio.[h]	77	0.040
Poly(vinyl chloride), iso.[h]	77	0.016
Poly(vinyl chloride), atactic[h]	77	0.013
Polytetrafluoroethylene[a]	130 (−113)	0.001–0.021

[a] Reference 29. [b] U. Suter and P. J. Flory, *Macromolecules*, **8**, 765 (1975). [c] D. Y. Yoon, P. R. Sundararajan, and P. J. Flory, *Macromolecules*, **8**, 776 (1975). [d] A. E. Tonelli, *Macromolecules*, **7**, 6232 (1974); **8**, 544 (1975); **10**, 633, 716 (1977). [e] A. E. Tonelli, *Macromolecules*, **5**, 558 (1972); **6**, 503 (1973). [f] P. R. Sundararajan and P. J. Flory, *J. Am. Chem. Soc.*, **96**, 5025 (1974). [g] A. E. Tonelli, unpublished results. [h] P. J. Flory and C. J. Pickles, *J. Chem. Soc., Faraday Trans 2*, **69**, 632 (1973).

The remainder ΔC^{misc} represents various additional modes of energy input which are required to raise the temperature of the liquid but not of the glass. Any mode of excitation which is normally allowed but is frozen in the glass can contribute to ΔC^{misc}. The heat capacity change arising, for example, from the change in the vibrational frequency or amplitude or from the change in the average nearest neighbor coordination number may be included in it, after proper allowance is made for the part that is attributable to the volume change. Frequently, ΔC^{misc} is assumed to be much smaller than the other two terms, but without adequate justification.

From the experimental ΔC_p, the free volume contribution ΔC^{fv} can be eliminated approximately by calculating the constant volume specific heat by means of the identity:

$$\Delta C_v = \Delta C_p - TV\Delta(\alpha^2/\beta) \qquad \text{(III.2)}$$

The difference $\Delta C_p - \Delta C_v$ is equal to ΔC^{fv} only approximately for the following reason. When the temperature of a glass is raised with the total volume kept constant, both the free volume and the core (occupied) volume presumably remain constant. With a liquid, however, the free volume and the core volume adjust themselves to seek a new minimum free energy under the constraint of the constant total volume.

Table II
Thermodynamic Data Used for the Calculation in Table III

Polymer	T_g, °C	V_g, cm^3/g	α_l, 10^4/°C	α_g, 10^4/°C	β_l, 10^5/bar	β_g, 10^5/bar	Ref
Polystyrene	89	0.97	5.34	2.50	5.33	3.31	24
Poly(methyl methacrylate), atactic	105	0.863	5.30	2.95	4.81	3.52	31
Poly(methyl methacrylate), isotactic	47	0.824	5.83	2.34	3.70	2.47	32
Poly(vinyl acetate)	30.7	0.843	6.03	2.35	5.01	2.99	33
poly(vinyl chloride)	80	0.75	3.76	1.61	3.99	3.04	20, 34

Table III
Comparison of Various Contributions to ΔC_p [a]

Polymer	ΔC_p (exptl)	Ref	$T_gV \times \Delta(\alpha^2/\beta)$	$T_gV \times (\Delta\alpha)^2/\Delta\beta$	ΔC_v (eq III.2)	$\Delta C_{v\tilde{v}}$ (eq III.3)	ΔC^{conf} (Table I)
Polystyrene	0.071	37	0.029	0.034	0.042	0.037	0.011–0.017
Poly(methyl methacrylate), atactic	0.070	36	0.026	0.033	0.044	0.037	0.009
Poly(methyl methacrylate), isotactic	0.111	36	0.044	0.062	0.067	0.049	0.013
Poly(vinyl acetate)	0.120	35	0.033	0.041	0.087	0.079	0.013–0.018
Poly(vinyl chloride)	0.068	21	0.017	0.031	0.051	0.037	0.013

[a] All in units of cal/(g deg).

The free volume contribution ΔC^{fv} can be eliminated completely from the experimental ΔC_p only by evaluating the specific heat $\Delta C_{v\tilde{v}}$ obtainable under the condition of constant total and constant free volume. $\Delta C_{v\tilde{v}}$ cannot be derived from thermodynamic data alone, however, because the condition of constant total and free volume does not represent an equilibrium situation attainable by experiment. Recently Nose[25] discussed a hole theory of liquids and glasses and showed that the following relation can be derived from his model:

$$\Delta C_{v\tilde{v}} = \Delta C_p - TV(\Delta\alpha)^2/\Delta\beta \qquad \text{(III.3)}$$

In the following we will utilize eq III.3 as a means of evaluating approximate values of $\Delta C_{v\tilde{v}}$ for real liquids from experimental values of ΔC_p, $\Delta\alpha$, $\Delta\beta$, etc.

We now have two methods by which the sum of the two terms $\Delta C^{conf} + \Delta C^{misc}$ in eq III.1 can be estimated: (1) by means of ΔC_v evaluated according to eq III.2, and (2) by means of $\Delta C_{v\tilde{v}}$ which can be evaluated approximately by eq III.3. By comparing such estimates with the theoretical conformational specific heats computed from the RIS model, we plan to assess the relative magnitude of the ΔC^{misc} term.

Table II summarizes the experimental values, obtained from the literature, of the various quantities required for evaluation of ΔC_v and $\Delta C_{v\tilde{v}}$ by eq III.2 and III.3. There are not many polymers for which β_l and β_g are known to satisfactory accuracy. Recently, the Tait relation

$$1 - V(T,p)/V(T,p_0) = 0.0894 \ln \left[1 + (p - p_0)/B(T)\right] \qquad \text{(III.4)}$$

was shown[30] to describe pressure–volume–temperature data of polymer liquids and glasses well. Only those polymers for which the Tait parameter $B(T)$ was evaluated accurately from experimental data are included in Table II, and the values of β_l and β_g are those obtained by differentiation of eq III.4.

Table III compares the experimental ΔC_p values from the literature with ΔC_v and $\Delta C_{v\tilde{v}}$ calculated according to eq III.2 and III.3. The free volume contribution, ΔC^{fv}, approximated by $T_gV\Delta(\alpha^2/\beta)$ and $T_gV(\Delta\alpha)^2/\Delta\beta$, is seen to comprise roughly a third to a half of the total magnitude of ΔC_p. In the last column of Table III are reproduced the conformational specific heats C^{conf}, from Table I, which were calculated on the basis of the RIS model of polymer conformation. They are generally much smaller than ΔC_v or $\Delta C_{v\tilde{v}}$, which according to our discussion above should consist of two terms, the conformational specific heat and the miscellaneous contribution to ΔC_p from various unaccounted sources. Thus, the results shown in Table III contradict two often-expressed views: that the experimental ΔC_p values arise mostly from the freeze-in of the free volume and the polymer conformation in the glass and that there is no difference between the liquid and the glass with respect to vibration or any other modes of thermal excitation. In a recent article[37b] O'Reilly analyzed experimental ΔC_p data for a number of polymers on the very assumption that ΔC_v is indeed equal to the conformational specific heat. The values of the "flex" energy (the energy difference between two assumed conformational states of a polymer chain) which he evaluated on this basis would therefore contain the effect of other contributions to the specific heat which we term miscellaneous.

Besides volume and enthalpy, many other properties exhibit an abrupt change in their temperature coefficients at T_g. For example, the infrared absorbance of polystyrene, at a number of frequency bands corresponding to the motions of the chain backbone and the phenyl group, were shown[38] to undergo marked changes in their temperature dependence at T_g. The frequency and amplitude of infrared-active vibrational modes are expected to be influenced by the intermolecular force field, and therefore the observed change in the temperature coefficients at T_g may arise partly from the change in the thermal expansion coefficient. However, Hannon and Koenig[39] found that such changes in the temperature coefficients of infrared absorbance were also found at the β transition temperature of poly(ethylene terephthalate) at which no discernible break in the thermal expansion coefficient was observed. The commonly held view that the vibrational heat capacity is not affected by the onset of the glass transition has therefore to be questioned.

Recently, Goldstein[40] made a detailed analysis of the specific heat data obtained by Chang and others[41,42] on several polymeric and nonpolymeric glasses and concluded that, on the average, only about half of the ΔC_p observable at T_g can be attributable to the configuration effect. He argues that the rest of the ΔC_p arises from such sources as the changes in anharmonicity, in the number of secondary relaxation degrees of freedom, or in vibrational frequencies due to the difference 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

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Received September 16, 1977

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

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

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

0024-9297/78/2211-0117$01.00/0