Polymer Vol. 38 No. 13, pp. 3263–3268, 1997
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0032-3861/97/$17.00 + 0.00

S0032-3861(96)00895-6

Enthalpy relaxation in glassy polystyrenes: 2

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(Received 19 December 1995)

The changes in enthalpy (ΔH_∞) between the experimental glass and the fully relaxed glass for two polystyrene samples of different molar masses have been estimated using the Cowie–Ferguson approach. These were then compared with the change predicted by a simple two-state conformational energy expression for the specific heat increment at constant volume. Comments on the nature of allowed motions in the glass are made. © 1997 Elsevier Science Ltd.

(Keywords: enthalpy relaxation; physical ageing; equilibrium glass)

INTRODUCTION

Thermodynamic behaviour at the glass transition

In the first paper of this series[1] the enthalpy behaviour of a polymer near its glass transition (T_g) was discussed. Extrapolation of the liquid state enthalpy into the glassy region leads to the Kauzmann[2] paradox whereby a liquid is predicted to have a lower heat content than the crystalline solid. This difficulty arises because thermodynamic behaviour is projected through a transition viewed as entirely kinetic in nature and Gibbs[3] outlined a resolution to the paradox on the basis of the quasi-lattice Flory model[4] for the bulk polymer. In this, the expression for the number of configurations (W) which are available to a flexible polymer chain, i.e. one which is characterized by two different conformational states separated by an energy difference $\Delta\varepsilon$, becomes unity when $\Delta\varepsilon/k = 1.27\,T$, where T is the temperature in Kelvins and k is the Boltzmann constant. Below this temperature the configurational entropy ($k \ln W$) is illogically negative.

The statistical mechanical elaboration of this idea was given in a series of papers by Gibbs, DiMarzio and their coworkers[5–8] defining a temperature $T_2 < T_g$ at which a flexible polymer chain has achieved one of a degenerate set of states corresponding to configurations of lowest permissible energy. T_2 is a true (Ehrenfest) second-order transition and correctly reproduces such properties as the variation of T_g with molar mass and with the mole fraction of a plasticizer. The experimentally accessible kinetic 'quasistatic' glass transition temperature T_g is of course distinct from T_2, being the temperature at which relaxation times have values too long to permit structural reequilibration; but even this behaviour itself is deemed to be a reflection of the decreasing opportunities available to the system as the configurational entropy approaches zero.

At the temperature T_2 and below, therefore, the slope of the enthalpy vs temperature *must* be less than that extrapolated from the liquid region since now it reflects only changes in internal energy which are not associated with configurational readjustment. However, in the region immediately below T_g, and given long enough observation times, do thermodynamic variables characterize true liquid behaviour?

Enthalpy recovery

Above T_g a polymer is free to explore any and all configurations appropriate to its instantaneous temperature. On cooling towards T_g the total number of available configurations rapidly reduces, i.e. the chain effectively 'stiffens' as the temperature approaches $\Delta\varepsilon/k$. If vitrification is idealized as a single temperature, then immediately above T_g a polymer has complete rotational mobility about main chain-bonds and is in conformational equilibrium with its surroundings. On passing through T_g this set of conformations is frozen, and any further cooling produces a glass not in conformational equilibrium with its surroundings, having an enthalpy in excess of that appropriate to the lower temperature and towards which it will relax if kinetically able so to do. Enthalpy relaxation in a metastable experimental glass thus involves the gradual loss of excess configurational energy.

The evolution of enthalpy loss in a glass with the ageing time t_a has been measured[1] for a series of 4-substituted polystyrene polymers and discussed with respect to various multiparameter (MP) theories[9–19] and the alternative Cowie–Ferguson approach[20–22] which uses the Williams–Watts function in the form

$$\Delta H(t_a) = \Delta H_\infty\{1 - \exp[-(t_a/\tau)^\beta]\} \qquad (1)$$

The relaxed enthalpy $\Delta H(t_a)$ obtained after a period t_a of isothermal ageing is evaluated from

$$\Delta H(t_a) = \int_{T_a}^{T_b} \Delta Cp(T)\,\mathrm{d}T \qquad (2)$$

where $\Delta Cp(T)$ is the difference between the heat capacities of the aged and the unaged sample between two convenient limits.

The parameters β and τ of equation (1) showed no correlation with substituent structure in the series of polystyrenes and, apart from poly(4-hydroxystyrene),

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the total enthalpy relaxed ΔH_∞ was also broadly similar for all the samples. Although there is justifiable argument over whether β and τ are 'pure' kinetic parameters, which may or may not be structure specific, the total amount of relaxable enthalpy must indicate a distinct thermodynamic condition and should be more amenable to prediction from a model of the glassy state.

Conformational contributions to specific heat

ΔCp, the difference between liquid and glass heat capacities, reflects the freezing of molecular motion and some proportion of this (C_{conf}) must be due to the mobile conformational equilibrium that pertains in the liquid state. O'Reilly[23,24] proposes that C_{conf} can be identified directly with ΔCv, the heat capacity difference between the glass and liquid at constant volume. This conformational contribution may be calculated from the standard relation

$$\frac{C_{\text{conf}}}{R} = \frac{(\Delta\varepsilon/RT)^2 g' \exp(-\Delta\varepsilon/RT)}{[1 + g'\exp(-\Delta\varepsilon/RT)]^2} \tag{3}$$

where $\Delta\varepsilon$ is the energy difference between *gauche* and *trans* conformations of the polymer backbone and g' is the ratio of the degeneracies of the upper (*gauche*) state to the lower (*trans*) state. The usual thermodynamic relationship between Cp and Cv then leads to

$$\Delta Cp(T) = C_{\text{conf}} + \left\{\frac{TV_1\alpha_1^2}{\gamma_1} - \frac{TV_g\alpha_g^2}{\gamma_g}\right\} \tag{4}$$

V is the specific volume, α_i and γ_i are the isobaric expansivity and isothermal compressibility* respectively, and subscripts l and g refer to the liquid and glassy states. Equations (3) and (4) have been utilized to deduce $\Delta\varepsilon$ from experimental values of ΔCp at T_g for a number of polymers[23,24].

An alternative connection can however be made: equation (2) is quite general and by inserting $\Delta Cp(T)$ from equation (4) above we obtain

$$\Delta H_\infty(T_a) = \int_{T_a}^{T_g} C_{\text{conf}}\,dT + \int_{T_a}^{T_g}\left\{\frac{TV_1\alpha_1^2}{\gamma_1} - \frac{TV_g\alpha_g^2}{\gamma_g}\right\}dT \tag{5}$$

which relates the total enthalpy relaxation with the heat capacity difference implied by equation (3). To be more precise, equation (5) predicts the total enthalpy recoverable, both by relaxation of conformations frozen in at T_g and, since the term in braces may be interpreted in terms of free volume[23], the concurrent relaxation of the excess hole fraction frozen in at T_g.

It is the purpose of this paper to explore the utility of equation (5) by comparison with ΔH_∞ data for polystyrene using literature p–V–T data along with an appropriate value for $\Delta\varepsilon$ estimated from conformational energy calculations.

EXPERIMENTAL

Polymer samples

One of the polystyrene samples (PS37k) has already been described[1]. A second polystyrene with molar mass $2.67 \times 10^5\,\text{g mol}^{-1}$ (PS267k) and polydispersity 1.07 was supplied by the Dow Chemical Company (Midland, USA); the enthalpic T_g of this sample was 376.8 K.

Determination of ΔH_∞ values

The ageing behaviour for PS267k is shown in *Figure 1*, that for the other sample has already been presented[2]. *Figure 1* shows that for ageing temperatures $\sim (T_g - 10\,\text{K})$ or less ΔH_∞ is achieved within experimental times, below these temperatures ΔH_∞ is estimated by extrapolation using the Cowie–Ferguson expression as before[20,21]; the data for PS267k are collected in *Table 1*.

CONFORMATIONAL ENERGY CALCULATIONS

The conformational energies of polystyrene have been examined by Flory and his coworkers[25] with a view to determining statistical weight matrices and configuration dependent properties such as the characteristic ratio. These were derived for meso (m) and racemic (r) diad segments so here it was decided to extend the segment modeling the polymer chain by examining a methyl-terminated tetramer.

There are six distinguishable tetramers, definable in terms of consecutive diads. These are shown in *Table 2* along with their Bernoullian probabilities. The optimum geometries of each of these were obtained by minimizing the total energy of the molecule using the program MMP2[26]. Flory concluded that the environment of the pendant phenyl groups is highly restrictive, and that the angle defined by the phenyl ring and the plane of the backbone carbons lies always within a few degrees of zero. However, contrary to this previous work, we have chosen not to freeze this angle at zero in our minimizations. *Figure 2a* shows as an example the

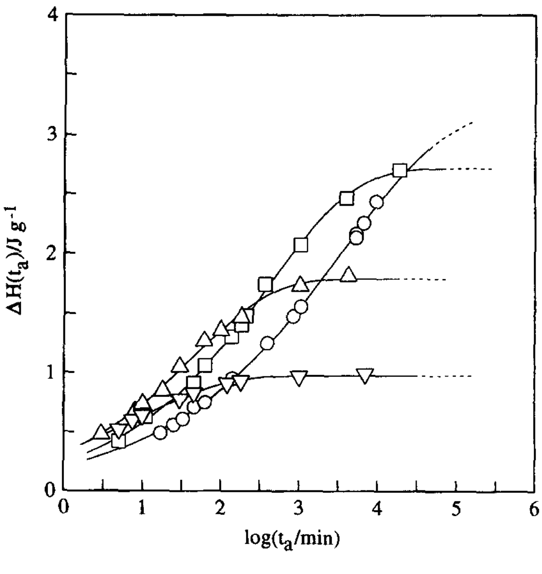

Figure 1 Ageing data $\Delta H(t_a)$ for PS267k at $T_g - T_a = 6.8$ K (inverted triangles); $T_g - T_a = 11.8$ K (triangles); $T_g - T_a = 16.8$ K (squares); $T_g - T_a = 21.8$ K (circles). The full lines are the Cowie–Ferguson function fitted as described in the text

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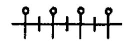
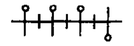
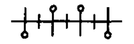
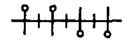
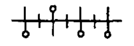
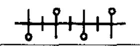
* Here we use the symbol γ to represent the isothermal compressibility instead of the more usual β in order to avoid confusion with the exponent in the Cowie–Ferguson equation

Table 1 Parameters from $\Delta H(t_a)$ fit to equation (1) for PS267k

T_a/K	$(T_g - T_a)$/K	ΔH_∞/J g^{-1}	log (τ/min)	β
370.0	6.8	0.98	0.96	0.39
365.0	11.8	1.79	1.64	0.43
360.0	16.8	2.71	2.59	0.39
355.0	21.8	3.22	3.57	0.33

Table 2 Configurations of a styrene tetramer

Diad sequence	Projection	p_{iii} ^{a}
mmm		p_m^3
mmr		$2p_m^2(1-p_m)$
rmr		$p_m(1-p_m)^2$
mrm		$p_m^2(1-p_m)$
rrm		$2p_m(1-p_m)^2$
rrr		$(1-p_m)^3$

^{a} p_{iii} is the probability of a given tetramer sequence iii and p_m is the probability that a polymer chain will add the next monomer unit in the same configuration as the last one at its growing end

minimized geometry ($\varepsilon_t = -19.35$ kJ) obtained for the *mmm* tetramer in the all-*trans* (isotactic) conformation.

Four *gauche* conformations of each tetramer were generated by rotation of the two mid-backbone bonds defined by carbon atoms 3-4-5-6 and 4-5-6-7 (*Figure 2*), each by +120° (g^+) and −120° (g^-), and these resulting geometries were allowed to minimize. *Figure 2b* shows the minimized geometry ($\varepsilon_g^+ = -3.51$ kJ) for the *mmm* tetramer in the g^+ conformation about bonds 3-4-5-6; *Figure 2c* shows the minimized geometry ($\varepsilon_g^- = -4.32$ kJ) for the g^- conformation about bonds 4-5-6-7.

Pairs of *gauche* conformations turn out to be identical, or are mirror images of each other, and should be isoenergetic (these are indicated in *Table 3*). MMP2 actually calculates these formally identical minima to be on average within 0.4 kJ of each other, possibly this reflects the scope for minor configurational divergence at either end of the tetramer in response to different starting geometries. The results of all the minimizations are collected in *Table 3*; the second column gives the energy (ε_t) of the all-*trans* configurations, whereas the remaining columns give $\Delta\varepsilon$, the difference between the all-*trans* and the indicated *gauche* conformation.

The tetramer model confirms the intuitive view that, in general terms, the polystyrene chain has access to two distinct conformational states, a low energy *trans* state and two higher energy *gauche* states [$g' = 2$ in equation (2)], with an overall average separation (the so-called flex energy) of $\Delta\varepsilon = 10.5$ kJ mol^{-1} from our calculations here. Three of the $\Delta\varepsilon$ entries in *Table 3* (one for *mmr*, two for *rmr*) are significantly lower than the others, indicating *gauche* environments in a central *meso* diad of almost equal energy to those of the *trans*. Flory and his coworkers[25] found such a low value for a single *meso* diad, but extending the model to a tetramer has a significant effect where in the *mmm* structure the *gauche* environments are of much higher energy than the *trans*.

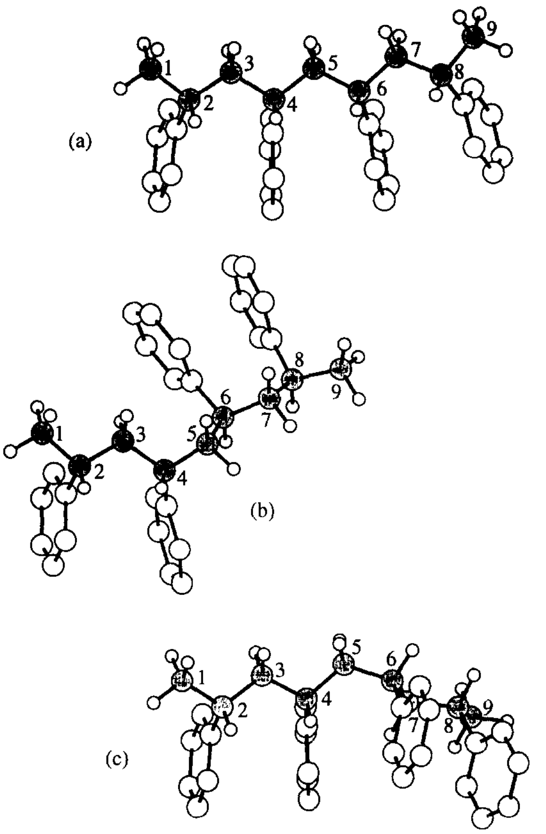


Figure 2 Minimum energy structures for a *mmm* tetramer of polystyrene chain. Main chain carbon atoms numbered as shown. (a) All-*trans*; (b) g^+ conformer about bonds 3-4-5-6; (c) g^- conformer about bonds 4-5-6-7

The values in the table refer to a hypothetical isolated chain segment where all intramolecular potentials are unperturbed by neighbour interactions. The bulk liquid environment presents a very different state of affairs but, as has been eloquently argued by Flory[27], although the instantaneous local environment undoubtedly perturbs any given bond, these perturbations are random and the averaged effect is effectively zero. On this basis we feel justified in using the flex energies calculated above to estimate conformational heat capacity contributions in the condensed state.

RESULTS AND DISCUSSION

Equation of state data

The specific volume, isothermal compressibility and expansion coefficient for polystyrene were obtained from the p-V-T study of Simha and Quach[28] whose $V(p)$ isothermal data were fitted a set of quadratics ln $V = a + bp + cp^2$, and γ evaluated as $-\partial \ln V/\partial P$ at $p = 1$ atm. Above and below T_g the isothermal compressibilities are best represented as linear functions

$$10^{10}\gamma_l/\mathrm{Pa}^{-1} = (4.85 \pm 0.37) + (1.16 \pm 0.24) \times 10^{-2}(T\,°\mathrm{C}^{-1}) \qquad (6)$$

$$10^{10}\gamma_g/\mathrm{Pa}^{-1} = (2.63 \pm 0.03) + (0.69 \pm 0.05) \times 10^{-2}(T\,°\mathrm{C}^{-1}) \qquad (7)$$

Table 3 Energies of minimised tetramer conformations

		$\Delta\varepsilon/\text{kJ mol}^{-1}$			
		3–4–5–6		4–5–6–7	
Pentamer	$\varepsilon_t/\text{kJ mol}^{-1}$	+120	−120	+120	−120
mmm	−19.35	15.86*	7.98#	7.48#	15.03*
mmr	−16.95	13.69	7.93	0.57	15.13
rmr	−14.53	13.06*	0.83#	1.17#	12.93*
mrm	−16.99	12.93*	11.56#	11.93*	11.42#
rrm	−16.48	14.15	12.68	10.92	9.98
rrr	−15.02	11.61*	10.30#	11.48*	10.24#

and * indicate energetically equivalent conformations

Table 4 Equation of state data for polystyrene

T_g/K	$V(T_g)/\text{cm}^3\,\text{g}^{-1}$	$10^4\alpha(T_g)/\text{K}^{-1}$	$10^{10}\gamma(T_g)/\text{Pa}^{-1}$
372.0_5 [a]	0.977_5 [a]	5.1_2 3.0_1	6.0 (liquid) 3.3 (glass)

[a] Intersection of $V(T)$ from above and below the transition region

Considerable scatter, especially above T_g, is reflected in the standard errors indicated. The specific volume exhibits quadratic behaviour above and below the transition region and the expansion coefficients $(\partial \ln V/\partial T)_{p=1\,\text{atm}}$ are given by

$$\alpha_l/\text{K}^{-1} = 5.11 \times 10^{-4} + 1.35 \times 10^{-8}(T\,°\text{C}^{-1}) \qquad (8)$$

$$\alpha_g/\text{K}^{-1} = 1.78 \times 10^{-4} + 1.22 \times 10^{-6}(T\,°\text{C}^{-1}) \qquad (9)$$

The values of the equation of state parameters evaluated from equations (6)–(9) at the glass transition are shown in *Table 4*.

Free volume relaxation

The second integral on the r.h.s. of equation (5), which is the free volume component of the relaxed enthalpy, becomes

$$\Delta H_\infty^{(\text{fv})} = \tfrac{1}{2}V(T_g)(T_g^2 - T_a^2)\left\{\frac{\alpha_l^2(T_g)}{\gamma_l(T_g)} - \frac{\alpha_g^2(T_g)}{\gamma_g(T_g)}\right\} \qquad (10)$$

when the temperature variation of all the parameters is ignored* and their values at T_g chosen instead. For example, with $T_g = 373\,\text{K}$, $\Delta H_\infty^{(\text{fv})}$ at an ageing temperature of $T_g - 10\,\text{K}$ is $0.60\,\text{J g}^{-1}$, with a confidence estimated at ±15%.

That the terms inside the braces in equation (4) (equal to ΔC_{fv}) do indeed represent free volume effects derives from the assumption that the specific heat change at constant volume is entirely conformational in origin (i.e. $\Delta Cp - \Delta Cv = \Delta C_{\text{fv}}$). Roe and Tonelli[29] have argued that this difference should be evaluated under the (unattainable) condition of constant total volume *and* constant free volume, and commend instead the alternative expression

$$\Delta C_{\text{fv}} = TV(\Delta\alpha)^2/\Delta\gamma \qquad (11)$$

based on Nose's hole theory of glass forming liquids[30]. Use of equation (11) for ΔC_{fv} gives the same numerical estimate for $\Delta H_\infty^{(\text{fv})}$ as above, but with an amplified uncertainty inherent in the ratio of small differences.

Equation (10) can in fact also be deduced from the Gibbs–DiMarzio configurational entropy theory of the glass transition as elaborated by DiMarzio and Dowell[31] who introduced an Einstein-type vibrational partition function assuming that, in part, the heat capacity is derived from (lattice) vibrational motions. Using the various substitutions and approximations provided, their equation (31) assumes the same form as equation (4), but now the terms within the braces carry the added interpretation of quantifying also the effects of changes in characteristic lattice frequencies, both from temperature dependent force constants and from conformational and free volume changes at the glass transition. $\Delta H_\infty^{(\text{fv})}$ for polystyrene is plotted as a function of ageing temperature in *Figure 3* according to equation (10) and using the data in *Table 4*. Adopting either of the other approaches, and interpretations, generates essentially the same dependence on T_a, well within the limits of ±15% imposed by the input data.

Conformational relaxation

Integration of the first term in equation (5) gives

$$\Delta H_\infty^{(\text{conf})} = \left.\frac{\Delta\varepsilon}{1 + g'\exp(-\Delta\varepsilon/RT)}\right|_{T_a}^{T_g} \qquad (12)$$

This contribution can be evaluated separately for each of the two rotated bonds in each tetramer, with their average taken to represent $\Delta H_\infty^{(\text{conf})}$ per mole of backbone bonds having that modelled sequence. The $\Delta\varepsilon$ for each of the two rotated bonds were themselves taken as the average† of the appropriate $g+$ and $g-$ energies and setting $g' = 2$ for all but the 4–5–6–7 bond in the *mmr* sequence and both bonds in the *rmr* sequence. These latter, each with one very low *gauche* conformation, were assigned a doubly degenerate ground state ($g' = 0.5$) with a single higher energy state. The $\Delta H_\infty^{(\text{conf})}$ contributions calculated from equation (12) for each of the tetramer sequences should be weighted by the value of p_{iii} (*Table 2*) appropriate to the polymer stereostructure considered. The

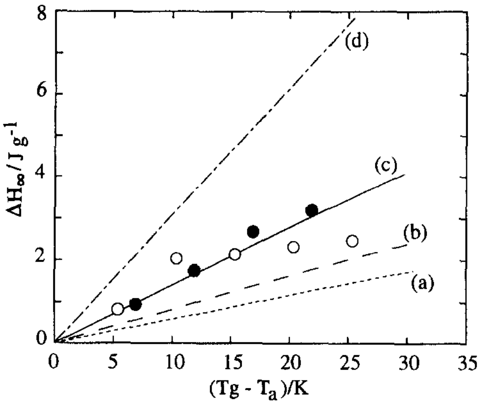


Figure 3 ΔH_∞ as a function of $T_g - T_a$ for polystyrene: line (a) $\Delta H_\infty^{(\text{fv})}$; line (b) $\Delta H_\infty^{(\text{conf})}$; line (c) $\Delta H_\infty^{(\text{fv})} + \Delta H_\infty^{(\text{conf})}$; line (d) $\Delta H'$. Experimental data: open circles PS37k; filled circles PS267k.

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* The use of equations (5) and (7) to describe $\alpha_l(T)$ and, especially, $\beta_l(T)$ significantly below T_g was deemed unreliable due to the large and increasing uncertainty in the extrapolation.

† Equation (3) is a good approximation to the exact statistical thermodynamical expresion for two non-degenerate upper states. In the worst case of the *mmm* tetramer, where there is a 66% variation of the g^+ and g^- energies form the average value used, the resulting difference in $\Delta H_\infty^{(\text{conf})}$ is only 2.4%

tetramer distributions in the polystyrene samples were not measured and in *Figure 3* we chose to show the $\Delta H_\infty^{(\mathrm{conf})}$ for $p_\mathrm{m} = 0.25$ which represents an $\sim 80\%$ syndiotactic chain—a reasonable expectation for the polymers used here.

It is interesting that the model calculations indicate that the conformational contribution to enthalpy should vary with tacticity; for example the respective values of $\Delta H_\infty^{(\mathrm{conf})}$ at $T_\mathrm{g} - 10\,\mathrm{K}$ are 1.03, 0.95 and $0.75\,\mathrm{J\,g^{-1}}$ for the syndiotactic ($p_\mathrm{m} = 0$), isotactic ($p_\mathrm{m} = 1$) and heterotactic ($p_\mathrm{m} = 0.5$) forms of polystyrene. To our knowledge, no study of enthalpy ageing has yet been carried out which confirms that such a difference indeed exists.

The relaxed glass

The total enthalpy relaxable from both free volume and conformational sources ($\Delta H_\infty^{(\mathrm{conf})} + \Delta H_\infty^{(\mathrm{fv})}$) is shown in *Figure 3* along with $\Delta H'$ which is the direct extrapolation of the liquid state enthalpy behaviour into the glassy state. The experimental values of ΔH_∞ are considerably less than $\Delta H'$, being approximately one half of this extrapolation at any temperature below T_g and, although the data exhibit more scatter than would be expected (or desired) from the nominal precision of the fitting routines used to estimate ΔH_∞*, they are much better described by the theoretical contributions from both conformational and free volume relaxation. On this basis then, equilibration of a metastable experimental glass does not proceed towards the equilibrium state of the polymeric liquid at the same temperature, but rather towards one of the equilibrium configurational states of the glass with its associated reduced free volume.

The enthalpic inequality $\Delta H_\infty^{(\mathrm{conf})} + \Delta H_\infty^{(\mathrm{fv})} < \Delta H'$ is of course equivalent to the inequality $C_\mathrm{conf} + \Delta C_\mathrm{fv} < \Delta Cp_\mathrm{expt}$ which has been the subject of discussion by several authors and which is taken to imply that the discontinuity in the heat capacity at T_g results from more than the freezing in of configurational states and the associated free volume. O'Reilly[23,24] favours the idea that side chains contribute to ΔCp_expt in that they possess their own conformational freedom which would be suppressed if all motion is frozen at T_g. Arguments along this line would seem to be inapplicable to polystyrene where only limited torsional oscillation of the phenyl groups is permissible in the first instance. Other contributions to ΔCp_expt have been suggested but not precisely quantified; changes in the amplitude of any torsional libration on vitrification[32] is allowed within the context of the polystyrene structure, as is any freezing in of the liquid state nearest neighbour coordination at T_g[33].

Recoverable enthalpy must of course arise from states that readjust over time, and it does not follow that all motions or states giving rise to ΔCp_expt should be involved in relaxation. There can be little or no direct relaxation effect from what might loosely be described as a motional contribution to heat capacity, such as a lattice[31] or a spectroscopic[33,34] vibration or a torsional movement[32,†]. If these are altered on vitrification they presumably remain unchanged thereafter. A relaxation effect from such a contribution would imply that a population of characteristic amplitudes and frequencies pertaining to the liquid at $T > T_\mathrm{g}$ would gradually be recovered at $T < T_\mathrm{g}$ in the vitreous state—which itself is undergoing densification as the free volume relaxes. Roe and Tonelli's proposal[33] of frozen nearest neighbour coordination would be a relaxable component of enthalpy, but no such contribution seems required to fit the data presented here.

The glass transition can be viewed as a kinetic event separating the *different* equilibrium thermodynamic behaviour of a liquid and a glass. The picture of a glass as an 'infinitely slow' liquid is not totally appropriate. Of the various modes that contribute to ΔCp, either by being frozen or altered on vitrification, only those associated with configurational readjustments are necessary to describe the equilibrium glass in relation to the experimental glass.

Finally, we conclude that MP descriptions of enthalpy relaxation which identify the equilibrium glass enthalpy with that of the liquid at the same temperature are in error in this respect. The approach outlined in this paper provides an independent method of estimating ΔH_∞ as opposed to regression fitting or inappropriate extrapolations of liquid state behaviour to obtain so-called equilibrium conditions. Gomez and Monleón[36] have also recognized this within the context of their configurational entropy approach for the prediction of heat capacity curves. This phenomenological treatment incorporates expressions for $\Delta Cp(T)$, which in essence is regarded as a semi-adjustable parameter, and optimum fits to experimental data for polycarbonate glasses occur when $\Delta Cp(T)$ is $\sim 0.5 \Delta Cp_\mathrm{expt}$‡. Their view of the limiting state corresponding to this condition is somewhat different to ours however. They argue that the material, as a result of topological constraints, is unable to reach the 'true' equilibrium of the equivalent liquid.

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[*] This is discussed in ref. 1. We believe the best pragmatic estimate of the uncertainty in determining such parameters is the experimentally observed scatter. The result here is that there is no discernible effect of molar mass on ΔH_∞

[†] In the limit, torsional libration becomes hindered internal rotation. In a past publication[35] we successfully described the specific heat contribution from alkyl side chain movements with a modified classical description of this motion. There we believed the chains were short enough and had sufficient freedom to behave as isolated hindered rotors. Undoubtably hindered rotation occurs in the liquid state of a polymer and is associated with conformational readjustments. How coordinated and how extensive, in time and space, these movements are, and what thermodynamic contribution results, eludes description

[‡] Since $\Delta H(t_\mathrm{a})$ and ΔCp are connected via equation (2) this is equivalent to the present case where ΔH_∞ is approximately one half of $\Delta H'$

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