

Enthalpy relaxation in glassy polystyrenes: 1

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Enthalpy relaxation at temperatures below the glass transition has been measured for three substituted polystyrene samples and for one poly(α -methylstyrene) sample. The overall changes in enthalpy between the experimental glass and the fully relaxed glass (ΔH_∞) were estimated by fitting experimental data to the three-parameter Cowie–Ferguson expression. These were compared with enthalpy relaxation in polystyrene itself. There was no experimentally detectable effect from the *para* substituent on the progress of enthalpy loss in the samples. Poly(4-hydroxystyrene), however, was found to exhibit unexpectedly high values of ΔH_∞ . The utility of the Cowie–Ferguson approach with respect to multiparameter phenomenological kinetic expressions for enthalpy relaxation is discussed. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Polymers behave as liquids when temperature changes are made more slowly than the time scale required by the molecules to readjust themselves to their new equilibrium condition. When temperature changes are made at rates greater than the characteristic rate of motion the polymer behaves as a glass. Below the experimental glass transition (T_g) the polymer is no longer able to attain structural equilibrium within the time scale of the given experiment.

Conceptually at least it is possible to prevent a polymer from entering the vitreous state by cooling it sufficiently slowly. Almost half a century ago now Kauzmann¹ pointed out the paradoxical result of this procedure in which a polymer, initially in its liquid state, is cooled slowly enough to permit the liquid structure to remain in thermodynamic equilibrium with its surroundings, i.e. following the dashed lines 1' in *Figure 1*. By such an experiment a liquid, below T_g but still above absolute zero, is predicted to have a lower heat content than the crystalline solid. An acceptable resolution of this paradox in the case of non-crystallizing polymers was first hinted at by Gibbs² and subsequently developed by him and his coworkers in a series of well-known contributions on the subject of the glass transition^{3–5}. However, for present purposes† it is only necessary to note that the observed glass transition temperature depends on the cooling or heating rate imposed during experiments, and that all glasses formed at finite rates are in a non-equilibrium state. Thus, as in every situation where a system finds itself under stress, relaxation towards thermodynamic equilibrium can occur.

Studies on polymer glasses have generally focused on volume^{6,7}, mechanical^{8,9} and enthalpy relaxation. The temperature range within which relaxation can be

readily observed is limited to a small interval, normally ~ 20 K below T_g . There is evidence^{8,10} that physical ageing can occur outwith this narrow band and in general should be expected between T_g and the first secondary transition T_β . A number of thermoplastic materials should consequently have an ageing range which includes temperatures of practical application. Pragmatically however, experiments are carried out sufficiently close to the glass transition such that significant effects can be observed within a few hours or at the most a few days, and due to the convenience offered by modern scanning calorimeters the largest number of studies have been carried out on the enthalpic relaxation in glassy polymers^{6–18}.

Figure 1 shows the schematic behaviour of a polymer in the glass transition region where the experimental step in the heat capacity $\Delta C_p(T_g)$ corresponds to the enthalpic slope change characteristic of devitrification. At any temperature T_a below T_g the enthalpy difference $\Delta H'$ between the extrapolated enthalpy behaviour of the liquid and that of the glass is equal to the shaded area between the corresponding $C_p(T)$ lines as shown in the figure.

Above T_g a polymer is free to explore all states appropriate to the instantaneous temperature and so is in conformational equilibrium with its surroundings. At the idealized T_g shown in *Figure 1* this set of conformations is frozen and any further cooling produces a glass not in conformational equilibrium with its surroundings, having an enthalpy, say point *x* in *Figure 1*, in excess of that appropriate to the liquid at the same temperature, and towards which it will relax if kinetically able so to do. The difference in enthalpy $\Delta H(t_a)$ between state *x* and some intermediate realisable state *y* reached after a period t_a of isothermal relaxation can be evaluated from^{19,20}

$$\Delta H(t_a) = \int_{T_a}^{T_b} \Delta C_p(T) dT \quad (1)$$

Here $\Delta C_p(T)$ is the difference between the experimental

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† The concepts of the Gibbs–DiMarzio approach and their relation to enthalpic ageing are discussed in the following paper

heat capacities of the aged and the unaged sample and the integral is evaluated between the ageing temperature T_a and a convenient temperature limit T_b above T_g . From the argument above, changes in $\Delta H(t_a)$ reflect the gradual loss of excess configurational energy in the experimental glass.

Measurements of $\Delta H(t_a)$ have been undertaken primarily with the aim of exploring the kinetic nature of relaxation in the glassy state and testing various multiparameter phenomenological (MP) models for the process^{12-18,21,22}. The enthalpic ageing of a glass is believed to be a self-retarding phenomenon^{23,24} in which the characteristic relaxation time (τ) for the process is a structure (or time) dependent parameter, i.e. at any $T_a < T_g$

$$\Delta H(t_a) = f(\tau(\delta_H)) \quad (2)$$

where $\delta_H = H(t_a) - H_E$ is the distance of the instantaneous glass from the equilibrium glass (H_E). The functions forming the right hand side of equation (2) as adopted by various groups^{12-18,21,22} all assume, either explicitly or implicitly, a value for H_E , or equivalently ΔH_∞ which is the asymptotic value of $\Delta H(t_a)$ after sufficient length of time to allow complete enthalpy recovery. Here we deliberately avoid identifying $\Delta H'$ in Figure 1 with ΔH_∞ since, as was pointed out by Kovacs²⁵, kinetic responses depend on the departure from a real physical equilibrium and not from any extrapolation, e.g. as given by point z in Figure 1. Various authors^{20,21,26} have noted the discordance between such assumed extrapolated equilibrium values and those measured as such.

EXPERIMENTAL

Polymer samples

The polystyrene sample (PS37k) was a Pressure Chemical Company standard, poly(4-hydroxystyrene) (PHS) was obtained from Polysciences Inc. and the poly(α -methylstyrene) (P α MS) was a Polymer Laboratories Ltd standard sample. Poly(4-chlorostyrene) (PC1S) and poly(4-methylstyrene) (PMS) were synthesized using standard radical techniques from commercial (Aldrich) monomers. Molar masses were measured by gel permeation chromatography in terms of polystyrene equivalents. The characterization details are summarized in Table 1.

Calorimetry

Heat capacities were obtained using a Perkin-Elmer Model DSC-2 differential scanning calorimeter. Indium metal was employed for temperature calibration and the data were evaluated with respect to sapphire as heat capacity standard. Sample weights were between 8 and 14 mg and the unaged or 'standard' glass was formed by cooling at 40 K min⁻¹ to $T_g - 70$ K after holding for 10 min at $T_g + 50$ K to erase previous thermal history. Aged glasses were subjected to the same thermal treatment, but first cooled to the chosen T_a , held for the required t_a , then finally cooled to $T_g - 70$ K prior to the data acquisition heating scan. The structural thermal stability of the samples was monitored by recycling through the chosen thermal history several times without ageing. Both weight and T_g reached constant values after the fifth cycle, indicating that structural equilibrium was achieved.

Data were collected at 0.67 s intervals between $T_g -$

60 K and $T_g + 50$ K using a heating rate of 20 K min⁻¹. The heat capacity difference $\Delta C_p(T)$ was obtained by subtracting the data for an aged and standard glass and was subjected to a linear three-point smoothing routine before integration to give $\Delta H(t_a)$. Glass and liquid state heat capacity data were well-fitted by the linear function $C_p = a + bT$, enabling the corresponding $H(T)$ data obtained by integration to be extrapolated to give the enthalpic glass transition. This point of intersection is heating rate independent²⁷, thus giving a consistent definition of the glass transition temperature.

RESULTS

Primarily for the purpose of estimating the approach to equilibrium properties beyond the range of experimentally convenient times Cowie and Ferguson^{19,20} have proposed the following semi-empirical function to describe the isothermal enthalpy relaxed from an unaged ground state after a time t_a

$$\Delta H(t_a) = \Delta H_\infty [1 - \exp(-(t_a/\tau)^\beta)] \quad (3)$$

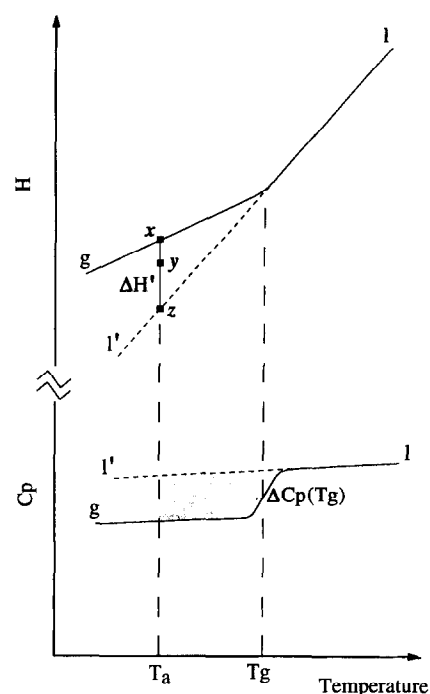


Figure 1 Behaviour of the enthalpy and heat capacity near the glass transition. Lines l and g are, respectively, the liquid and glassy states, dashed portions (l') are extrapolations of liquid behaviour below the glass transition. Other symbols are explained in the text

Table 1 Details of the polymer samples used

Polymer	$10^4 M_n$ (g mol ⁻¹)	M_w/M_n	T_g (K) ^a	$\Delta C_p(T_g)$ (J g ⁻¹ K ⁻¹) ^b	ΔT (K) ^c
PS37k	3.70 ^d	<1.06 ^d	373.0	0.28	4.5
PMS	3.5	2.5	381.5	0.26	6.5
PC1S	4.3	2.2	398.5	0.26	7.5
PHS	3.0 ^d	~2.5	433.0	0.48	14.0
P α MS	1.5	1.04	441.0	—	—

^a Enthalpic glass transition ± 0.5 K

^b Evaluated at enthalpic glass transition ± 0.03 J g⁻¹

^c Width of transition region ± 0.5 K

^d Manufacturer's data

Although the stretched exponential function $\phi(t) = \exp(-(t_a/\tau)^\beta)$ has been related to a relaxation spectrum²⁸ it is not an obvious expression for a self-retarding process. This deficiency has indeed aroused some criticism. Nevertheless, two of us have shown²⁹ from the statistical point of view that other models which utilize a time-dependent τ in order to describe adequately the thermal history dependence of $C_p(T)$ actually provide a no better, and at times a somewhat poorer, fit to experimental $\Delta H(t_a)$ data*.

The ageing measurements for the styrenic polymers presented here are fitted to equation (3) using the non-linear techniques previously described^{19,20} which employ the Levenberg–Marquardt algorithm³⁰. Two further advantages accrue from use of equation (3); having only three parameters it is ‘better behaved’ within a multi-parameter fitting routine and, although ΔH_∞ is obtained essentially by extrapolation†, this is not a direct extrapolation from the liquid state but one using glassy state data.

Polystyrene

Although ageing studies on PS are abundant in the literature, here it plays the role of a baseline. Since enthalpy relaxation appears to vary slightly with molar mass (Cowie and Ferguson, unpublished results), and to achieve a closer comparison with the modified styrene structures, it was decided to establish the enthalpy relaxation for PS of similar molar mass ($37\,000\text{ g mol}^{-1}$).

The ageing data obtained at five $T_a < T_g$ are shown in Figure 2 and the corresponding parameters of equation (3) are collected in Table 2. The significance of quoted standard errors, or uncertainties, in a set of fitted parameters obtained by non-linear routines is a matter of some conjecture³⁰. These are nominally expressions of confidence limits obtained from the goodness-of-fit indicator χ_{\min}^2 whereby parameter values are recalculated at $2\chi_{\min}^2$ and the differences between these and the values found at the minimum are used as an estimate of error. This, however, is more often a reflection of the curvature in χ^2 space in the region of the minimum. With regard to the ΔH_∞ entries in Table 2, we feel that the experimental uncertainty in $\Delta H(t_a)$ or the maximum deviation of $\Delta H(t_a)$ from the fitted line would be more appropriate—both are about the same and so we suggest they are at best read to $\pm 0.05\text{ J g}^{-1}$. Even accepting a greater uncertainty, these ΔH_∞ values are considerably less than the recoverable enthalpy predicted by extrapolating from above T_g .

Sufficiently close to the glass transition it appears (Figure 2) that a value very close to ΔH_∞ is reached during the experimental time scale, as was also found by others^{14,17,28}. Taking this as a direct measure of ΔH_∞ , equation (3) may be employed to obtain $\ln(\tau)$ as a function of t_a from the experimental $\Delta H(t_a)$ data for a fixed value of β . Although the choice of β is quite

arbitrary we undertake this exercise to discover which values will generate a dependence of $\ln(\tau)$ on δ_H in agreement with the precepts of MP theories referred to above, and Figure 3 shows the variation of $\ln(\tau)$ with $H(t_a) - H_E$ obtained with $\beta = 1.0$, 0.4 and 0.2 at $T_g - 5.3\text{ K}$. The positive slope as generated by $\beta = 0.2$ is physically unrealistic if τ is to retain any meaning as a kinetic parameter. However, if the assumption that $\Delta H' \equiv \Delta H_\infty$ is abandoned, and within the immediate context of allowing τ to be $\tau(\delta_H)$, equation (3) with β set equal to unity is equivalent to expressions employed by Petrie and Marshall^{16,17}, by Moynihan *et al.*¹¹ and by Narayanaswamy²⁴, in which a linear relation, with a negative slope, between $\ln(\tau)$ and δ_H is presumed. It can also be taken to represent the KAHR model equation³¹ with a single relaxation time. The set of $\ln(\tau)$ data

Table 2 Cowie–Ferguson parameters for PS37k

T_a (K)	$(T_g - T_a)$ (K)	ΔH_∞ (J g^{-1})	$\ln(\tau/\text{min})$	β
368.0	5.3	0.85	1.1	0.40
363.0	10.3	2.06	4.7	0.40
358.0	15.3	2.16	5.3	0.38
353.0	20.3	2.34	5.6	0.43
348.0	25.3	2.49	6.7	0.40

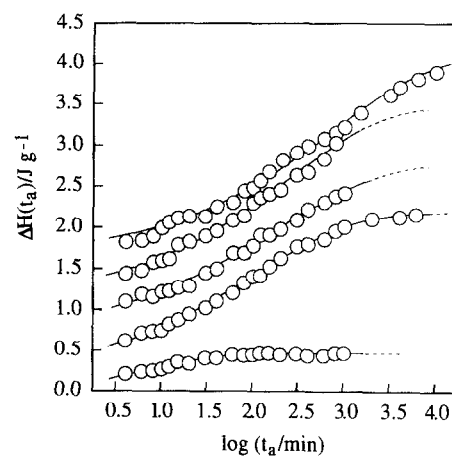


Figure 2 Measured enthalpy recovered as a function of ageing time for PS37k. Lowest curve is at $T_g - T_a = 5.3\text{ K}$, other curves are displaced vertically 0.5 J g^{-1} for $T_g - T_a = 10.3, 15.3, 20.3$ and 25.3 K .

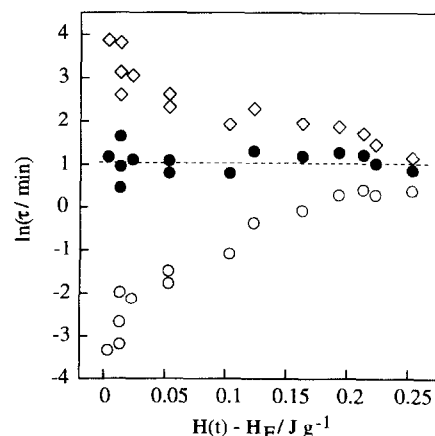


Figure 3 Values of $\ln(\tau)$ for PS37k calculated from equation (3) from the ageing data at $T_g - t_a = 5.3\text{ K}$. Diamonds, $\beta = 1.0$; filled circles, $\beta = 0.4$; open circles, $\beta = 0.2$. Dashed line drawn at $\ln(\tau) \approx 1.1$.

* In this paper the goodness of fit of data to equation (3) where τ was allowed to have a time dependence was compared with the case of a constant τ . It was unambiguously concluded that, when describing experimental enthalpy data, no better a fit was obtained. In such a case Occam's razor is rightly applied. This does not mean of course that τ is not a time-dependent parameter, but rather that $\Delta H(t_a)$ data do not reveal a time dependence and return what is actually a time-averaged value $\bar{\tau}$.

† In the sense that ΔH_∞ is almost always not a member of data set $\{\Delta H(t_a)\}$.

calculated with $\beta = 1$ shown in *Figure 3* deviate noticeably from the presumed linearity and in this sense MP theories must fail to give a completely accurate description of experimental behaviour.

The data from $\beta = 0.4$ appear to imply that τ is independent of the structural state of the system, as assumed by the Cowie–Ferguson approach. Although this approach does not impose any theoretical restrictions on β , structural independence would be a fallacious conclusion based on a circular argument. The relatively good representation of the ageing data by a zero-slope straight line in *Figure 3* is simply confirmation of the values of $\beta = 0.4$ and $\ln(\tau) = 1.1$ obtained from the non-linear fit to equation (3) in which they are assumed constants. Nevertheless, the obvious deviations of the individual $\ln \tau$ values from the dashed line in *Figure 3* may be a more realistic indicator of confidence in this parameter.

Poly(4-methylstyrene) and poly(4-chlorostyrene)

The results of ageing measurements on PMS and on PCIS are shown in *Figures 4* and *5*, and the Cowie–Ferguson parameters are collected in *Tables 3* and *4*, respectively. The overall picture of ageing response for these two substituted styrene polymers is remarkably similar to that of PS. Again, with temperatures in the approximate range $T_g - 20$ K, it is possible to define ΔH_∞ experimentally. These data also display $\ln(\tau)$ vs $H(t_a) - H_E$ behaviour similar to that shown in *Figure 3* for PS and discussed above.

The ageing data at their respective lowest ageing temperatures are less well defined for PMS and PCIS and consequently the corresponding parameter entries in *Tables 3* and *4* must carry a greater uncertainty. Even so, in terms of ageing behaviour, one is unable to discern any response to the structural and polar changes at the *para* position in the different samples. For example, *Figure 7* shows the Cowie–Ferguson β values for the series as a function of ageing temperature. No clear trend for any individual sample can be picked out and given the scatter of the data, all samples appear only to show that β may fall slightly with decreasing temperature. The corresponding plot for $\ln \tau$ is displayed in *Figure 8* and again only a general aggregate trend can be picked out; τ sensibly increases with increasing departure from T_g but with nothing to distinguish any individual effect from the *para* substituent. The corresponding increasing dispersion of the values of $\ln(\tau)$ from the drawn line, we believe, warn against placing too much confidence in values of this parameter when derived from incomplete ageing profiles well below T_g . Modest steric and polar changes at the side group, therefore, register no experimentally significant change in the relaxation behaviour of these styrenic structures.

Poly(α -methylstyrene)

The behaviour of this polymer at just one ageing temperature, $T_a = T_g - 10$ K, was obtained for comparison and is shown in *Figure 6*. The line is fitted with $\beta = 0.29$, $\ln(\tau/\text{min}) = 7.4$, with $\Delta H_\infty = 2.93 \text{ J g}^{-1}$ (346 J mol^{-1}). The relatively facile thermal degradation of P α MS made it difficult to acquire reproducible heat capacity scans with high molar mass samples in a thermal cycle that involved repeated heating to $T_g + 50$ K, and so a lower molar mass sample was employed to obtain these data for comparison with the styrene polymers

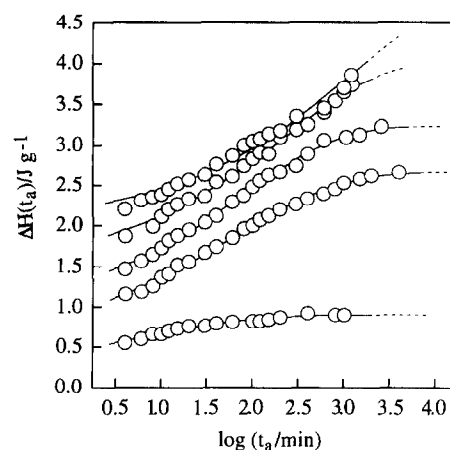


Figure 4 Measured enthalpy recovered as a function of ageing time for PMS. Lowest curve is at $T_g - T_a = 5.6$ K, other curves are displaced vertically 0.5 J g^{-1} for $T_g - T_a = 11.6, 15.6, 20.6$ and 25.6 K

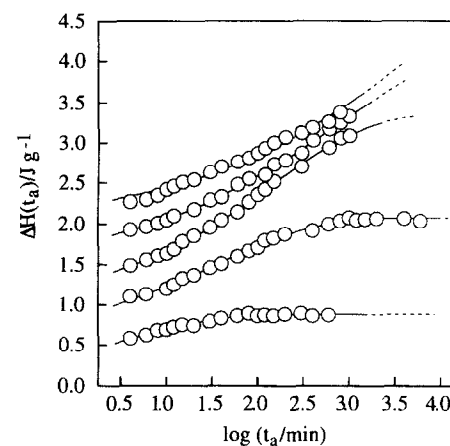


Figure 5 Measured enthalpy recovered as a function of ageing time for PCIS. Lowest curve is at $T_g - T_a = 5.6$ K, other curves are displaced vertically 0.5 J g^{-1} for $T_g - T_a = 10.5, 15.5, 20.5$ and 25.5 K

Table 3 Cowie–Ferguson parameters for PMS

T_a (K)	$(T_g - T_a)$ (K)	ΔH_∞ (J g^{-1})	$\ln(\tau/\text{min})$	β
376.0	5.6	0.90	1.3	0.37
370.0	11.6	2.16	4.1	0.36
366.6	15.6	2.29	4.6	0.41
361.0	20.6	2.53	6.9	0.41
356.0	25.6	2.95	7.1	0.38

Table 4 Cowie–Ferguson parameters for PCIS

T_a (K)	$(T_g - T_a)$ (K)	ΔH_∞ (J g^{-1})	$\ln(\tau/\text{min})$	β
393.0	5.5	0.88	1.2	0.42
388.0	10.5	1.58	3.6	0.39
383.0	15.5	2.37	5.0	0.41
378.0	20.5	2.70	6.6	0.34
373.3	25.5	3.15	8.3	0.31

above. Enthalpy relaxation takes a somewhat 'slower' profile for this structure and is characterized by the fit shown with a lower β and a higher $\ln(\tau)$ value than for the styrene structures already described. The total recoverable enthalpy for the P α MS glass, however, does not follow this pattern and the value of ΔH_∞ obtained is similar to that for PHS (below).

Poly(hydroxystyrene)

The ageing curves for this polymer are shown in Figure 9 and the Cowie-Ferguson parameters in Table 5. The behaviour of β and τ for PHS is included in Figures 7 and 8 where these parameters are best allocated to the same general trends followed by PS37k, PMS and PC1S. ΔH_∞ , shown collectively for all the samples in Figure 10 on a per mole basis, is however distinctly different. The

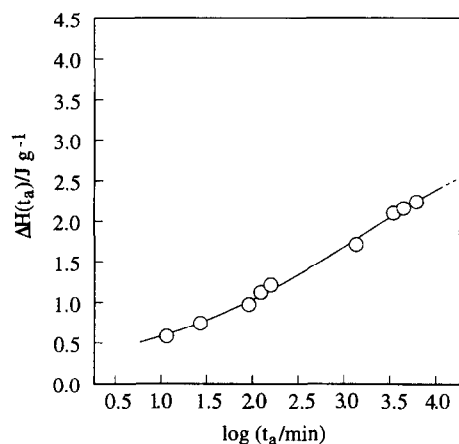


Figure 6 Measured enthalpy recovered as a function of ageing time for P α MS at $T_g - T_a = 10.0$ K

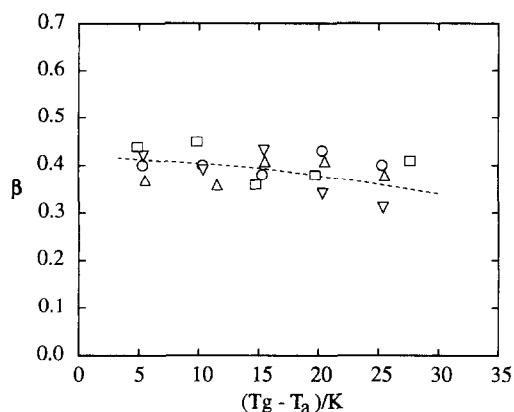


Figure 7 Values of β as a function of ageing temperature. Circles, PS37k; triangles, PMS; inverted triangles, PC1S; squares, PHS. Dashed line represents the general trend

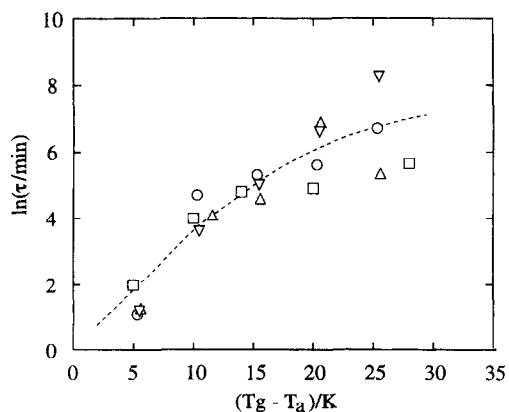


Figure 8 Values of $\ln(\tau)$ as a function of ageing temperature. Circles, PS37k; triangles, PMS; inverted triangles, PC1S; squares, PHS. Dashed line represents the general trend

magnitudes of ΔH_∞ for PS27k, PMS and PC1S increase in line with repeat unit molar mass, but PHS does not follow this trend, exhibiting values which are about 50% greater at any temperature than that of comparable PMS. The same deviation is just as apparent on a per gram basis as can be deduced by examining Tables 2-5.

DISCUSSION

The Cowie-Ferguson approach employs the Williams-Watts relaxation function³² to predict the equilibrium state towards which a metastable glass is evolving.

Table 5 Cowie-Ferguson parameters for PHS

T_a (K)	$(T_g - T_a)$ (K)	ΔH_∞ ($J g^{-1}$)	$\ln(\tau/\text{min})$	β
428.0	5.0	1.62	2.0	0.44
423.0	10.0	3.14	4.0	0.45
418.0	15.0	3.99	4.8	0.36
413.0	20.0	4.21	4.9	0.38
405.0	28.0	4.67	5.6	0.41

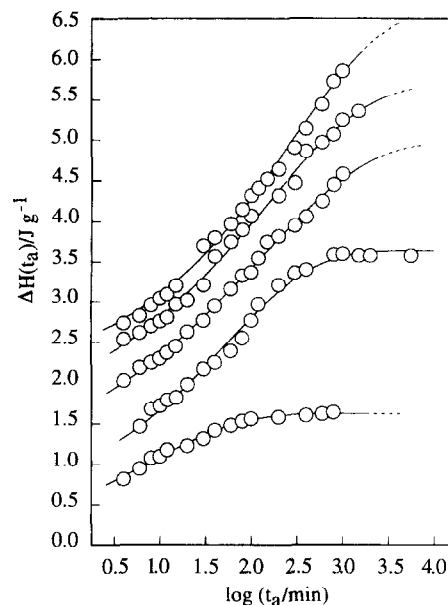


Figure 9 Measured enthalpy recovered as a function of ageing time for PHS. Lowest curve is at $T_g - T_a = 5.0$ K, other curves are displaced vertically $0.5 J g^{-1}$ for $T_g - T_a = 10.0, 15.0, 20.0,$ and 28.0 K

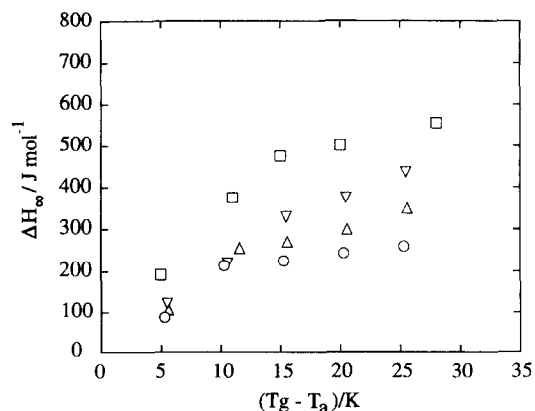


Figure 10 Values of ΔH_∞ as a function of ageing temperature. Circles, PS37k; triangles, PMS; inverted triangles, PC1S; squares, PHS

Mathematically this describes non-exponential behaviour in terms of a superposition of exponentially relaxing processes, and hence in terms of a distribution of relaxation times^{28,33}. As originally applied, the function was used to describe mechanical and dielectric relaxation data and, in the Cowie–Ferguson guise, appears also to be an adequate descriptor of non-linear structurally or time dependent data.

Hodge¹⁵ has stated emphatically that any reliable theory of ageing should invoke a structure sensitive time parameter $\tau(\delta_H)$, and this rationale is not disputed here. However two of us^{20,29} have shown that ‘reliability’, at least as far as fitting real data is concerned, is not lost by relaxing this requirement. Figure 3 illustrates this point; the best straight line fits to the $\ln(\tau)$ vs δ_H behaviour given either by $\beta = 1.0$ or 0.2 provide no better a description of the experimental $\Delta H(t_a)$ than $\ln(\tau) = 1.1$ (middle line in the figure). This type of exercise is described more fully in another publication²⁹ where it is concluded that the Cowie–Ferguson approach reproduces many experimental data with adequate precision without explicit structure dependence of the time parameter.

Is it reasonable to draw comparisons between the relaxation behaviour of the various styrenic polymers in terms of the β and τ parameters? In the Williams–Watts sense β may be taken as a measure of the width of the distribution of relaxation times and τ is the time when the relaxation function takes $1/e$ of its initial value. Comparisons with the structural parameters of MP theory are therefore not obvious, nor indeed may be proper. Nevertheless, although unable to express the conjoined effects of time (structure) and temperature, under a given set of conditions as here, the simple two-parameter relaxation function seems well able to describe the time evolution of enthalpy recovered—and hence it provides an adequate framework for comparison, as concluded by others³⁴. We believe the conclusion that the *para* substituent has little effect on the rate of physical ageing is just as readily drawn from Figures 7 and 8* as from any other data-fitting exercise.

Although there is only one temperature for comparison, the introduction of an α -methyl group results in $\ln(\tau)$ being significantly increased. Since τ arguably has a kinetic basis intuition this would suggest that this reflects higher energy barriers to molecular rearrangements during enthalpy recovery, which presumably include main chain rotation. Main chain ‘stiffness’ is traditionally related to the value of the T_g and on such a basis PHS would be expected to behave similarly to P α MS. This is obviously not the case here, and in general we have found that T_g and τ are uncorrelated³⁵ and that the latter parameter has an as yet uncovered dependence

on structure. The total relaxable enthalpy ΔH_∞ , however, should be independent of all and any internal barriers and is a more promising candidate for rationalization. Indeed a prescription to estimate ΔH_∞ , and its consequent elevation from the status of a fitted parameter, would appear worthwhile exploring from both the present viewpoint and also that of MP theories. It is this which we address in the next paper in this series.

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* Within the Williams–Watts formalism the average relaxation time $\langle\tau\rangle$ depends on both τ and β via $\langle\tau\rangle = (\tau/\beta)\Gamma(1/\beta)$ where $\Gamma(x)$ is the gamma function. The plot of $\ln(\tau)$ vs $T_g - T_a$ does not differentiate the various structures and indicates the same conclusion as was drawn from Figure 8