The glass transition behaviour and thermodynamic properties of amorphous polystyrene

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(Received 4 April 1989; accepted 20 April 1989)

The effect of molecular weight (MW) and thermal history on the heat capacity (c_p) of amorphous polystyrene over the temperature range from 200–440 K has been measured using differential scanning calorimetry (d.s.c.) General equations are given that show the influence of MW on c_p in both the glassy and liquid states. An enthalpic definition of the glass temperature reflects changes in the glass structure, due to thermal history, that are not found using conventional d.s.c. constructions. Thermodynamic and statistical mechanical theories give reasonable approximations to the observed T_g-MW curve but small systematic deviations are found. The effect of thermal history on T_g can be reproduced using a MW-dependent activation enthalpy.

INTRODUCTION

The structure of a glass is not unique. It is influenced by the rate (q) at which the molten equilibrium liquid is cooled into the glassy state, by any subsequent annealing and by mechanical stresses and strains. Because of this, the glass transition temperature (T_g) is also not unique but is a complex function of thermal and mechanical history. A particular glass may therefore be characterized by a T_g which is determined by the change in some thermodynamic parameter on heating into the equilibrium liquid state. For many years the most widely used parameter was the specific volume (V), using dilatometry[1], with T_g being defined by the temperature where V–T curves for the glassy and liquid states intersect. More recently differential scanning calorimetry (d.s.c.) has become widely used to characterize polymeric glasses: d.s.c. requires orders of magnitude less material than dilatometry and sample preparation is far less demanding. Against this must be set the fact that the d.s.c. signal is related to the heat capacity (c_p) of the sample rather than its enthalpy (H), the appropriate thermodynamic analogue of specific volume. In principle there is no problem in transforming c_p–T to H–T curves but this is rarely done and the kinetic effects that are common in the T_g region mean that the many geometrical constructions that are generally used to derive a d.s.c. value of 'T_g' are only significant for quality control purposes. If, for example, experimental conditions (heating rate, sample size and/or geometry) are changed but the original glass-forming conditions remain constant, 'T_g' also tends to change. Clearly the use of a common glass structure implies that all these particular samples should be characterized by a common T_g and this is the case when the correct enthalpic definition[2] of T_g is used.

In this paper the influence of molecular weight (MW) on the glass temperature of a series of anionic polystyrenes is examined using the enthalpic appoach to T_g. Special attention is paid to the effects of changes in q. The effect of MW on the thermodynamic properties of polystyrene is clearly shown and general equations are given.

EXPERIMENTAL

Polymers were n-butyl terminated anionic polystyrenes supplied by Polymer Laboratories Ltd, MW values ranged from 516 to 15 000 000 (*Table 1*) with $M_w/M_n <$ 1.10. Data supplied with the polymers gives the g.p.c. peak average MW (M_p) rather than the more relevant, for the present work, number average (M_n). Values of M_n were made available through the courtesy of D. F. Scholes, Polymer Laboratories (differences between M_p and M_n were only significant for low MW). Samples were freed from residual solvent by heating to constant weight at 440 K (400 K for MW < 1000) in open aluminium pans (which were then fitted with lids prior to the actual measurements) in the normal nitrogen atmosphere of the d.s.c.; 440 K was the maximum temperature used in subsequent experiments (except for the oligomers with MW < 1000 when 400 K was never exceeded). No changes in T_g could be detected on repeatedly cycling representative high and low MW polymers in the d.s.c. so that results were not influenced by thermal degradation.

Experiments were carried out using a Perkin Elmer DSC2 operating in the specific heat mode. Measurements were made on the empty sample pan, pan plus sample, and pan plus alumina calibrant[3]. Low temperatures were obtained using the Perkin Elmer variable temperature liquid nitrogen cooling accessary. Heating rates were 20 K min^{-1} and sample masses were about 20 mg. Data treatment used procedures developed in our laboratories

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Table 1 Heat capacities and glass temperatures of anionic polystyrenes

M_n	Heat capacity ($Jg^{-1}K^{-1}$)				$T_g(K)$ after cooling through T_g at $q\,K\,min^{-1}$			
	$c_{pg}=a+bT$		$c_{pl}=A+bT$		$q=-0.3125$	-5		-40
	a	$b(\times 10^3)$	A	$B(\times 10^3)$	$T_{gs}{}^a$	$T_{go}{}^b$	$T_{gs}{}^a$	$T_{gs}{}^a$
516	−0.092	5.06	0.862	2.88	240.5	244.0	244.0	–
628	−0.076	4.80	0.588	3.12	256.6	259.0	260.2	263.0
724	−0.086	4.80	0.575	3.14	267.5	271.3	271.2	274.0
840	−0.040	4.54	0.546	3.18	278.5	282.1	282.1	284.9
940	−0.102	4.70	0.725	3.12	286.0	288.6	289.5	292.4
1110	−0.110	4.70	0.703	3.15	296.1	303.7	299.7	302.5
1650	−0.094	4.58	0.710	3.11	317.2	324.4	320.7	323.5
2050^c	−0.076	4.50	0.687	3.17	326.5	326.5	329.9	332.7
2380	−0.090	4.50	0.692	3.14	332.0	337.3	335.2	337.9
3610	−0.135	4.64	0.707	3.09	344.2	347.4	347.4	349.7
3660^c	−0.097	4.47	0.659	3.19	344.5	346.3	347.6	350.0
4920	−0.177	4.74	0.681	3.14	350.6	354.4	353.7	356.0
7600	−0.096	4.46	0.722	3.04	357.4	360.3	360.4	362.8
8500	−0.151	4.60	0.728	2.98	358.7	361.7	361.7	364.0
10200	−0.131	4.56	0.714	3.06	360.6	363.3	363.6	365.9
10400^c	−0.043	4.26	0.586	3.36	360.7	363.4	363.7	366.0
11360	−0.131	4.50	0.667	3.12	361.5	364.0	364.5	366.8
12100	−0.085	4.40	0.631	3.24	362.1	363.2	365.0	367.3
16600	−0.151	4.62	0.738	3.00	364.4	367.3	367.3	369.6
19800	−0.052	4.32	0.730	3.02	365.6	368.3	368.6	370.8
21400	−0.122	4.52	0.719	3.02	365.9	367.5	368.9	371.1
26800	−0.084	4.38	0.620	3.24	367.0	367.8	370.0	372.2
68000	−0.130	4.50	0.720	3.00	370.2	373.1	373.2	375.4
195000	−0.109	4.46	0.652	3.20	371.5	375.2	374.5	376.7
490000	−0.110	4.44	0.639	3.22	371.9	375.3	374.9	377.1
1080000	−0.108	4.46	0.700	3.08	372.1	375.1	375.1	377.3
1750000	−0.047	4.23	0.594	3.32	372.2	374.5	375.2	377.4
2750000	−0.035	4.19	0.690	3.08	372.2	374.8	375.2	377.4
15000000	−0.126	4.48	0.636	3.22	372.2	375.7	375.2	377.4

^{a} Smoothed data (see text)
^{b} Observed data, $T_{go}-T_{gs}$ at other cooling rates is very similar
^{c} Sample from Pressure Chemical Company
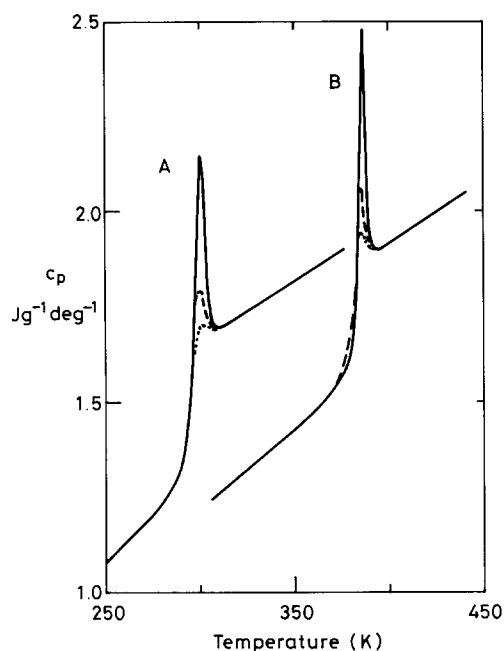
Figure 1 Heat capacity curves for anionic polystyrenes after cooling through the glass transition at 0.3125 (——), 5 (———) and 40 (····)$K\,min^{-1}$, heating rate $20\,K\,min^{-1}$. $M_n=940$ (curve A) or 2750000 (curve B)

to give specific heat capacity curves. Typical examples are shown in *Figure 1*.

Glasses were formed in the d.s.c. by cooling through T_g at a rate q, generally $q=-0.3125$, -5, and $-40\,K\,min^{-1}$; cooling was continued to at least 40 K below T_g so that

any subsequent isothermal annealing was insignificant. The slowest cooling was usually done overnight (with samples in both d.s.c. pans to save time). For the fastest cooling rate it was essential to start at a temperature high enough to ensure that the sample itself had actually attained the programmed rate before reaching T_g (this was about T_g+40 for $q=-40\,K\,min^{-1}$), the temperature ambient to the d.s.c had also to be low enough to maintain the appropriate q until at least T_g-40.

All runs were repeated with fresh material to check individual reproducibility. The large number of polymers investigated gave a good indication of the overall reproducibility.

RESULTS

The data collection system gave two or three points per degree and these were fitted to equations of the form $c_{pg}=a+bT$, $c_{pl}=A+BT$ (subscripts g and l refer to the glassy and liquid states respectively, inclusion of a quadratic term did not improve the fit). Data for the molten polymers gave no indication of the liquid–liquid transition which, it has been suggested[4], should be reflected by a change in the slope of the C_p vs. T curve at ca. 1.2 T_g; this is about 420 K for $M_n=5000$ so that the event should at least have been observable for polymers of lower MW. Thermal history had no effect on c_{pg} which is to be expected in view of the marginal (1 or 2%) difference, below T_g, between the heat capacity of a crystalline material and its quenched glass[5]. The parameters, a, b, etc. of *Table 1* are valid from 200 or 240 K to T_g-20 and from T_g+20 to 400 or 440 K where the lower figures refer to oligomers with $M_n<1000$.

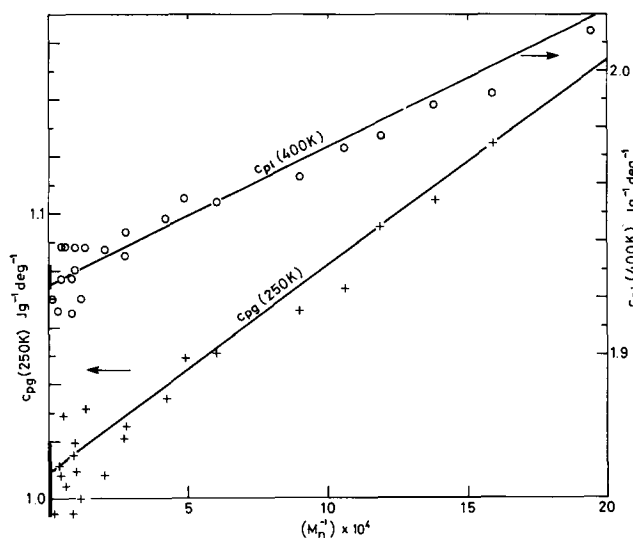**Figure 2** The effect of M_n on heat capacity at 250 (glass) and 400 (liquid) K; high M_n data are shown as a thickening of the ordinate. The lines are calculated according to equation (5) with the parameters of equations (6) and (8) (glass) or (7) and (9) (liquid)

$T_g \pm 20$ implies that for the thermal histories used here the glass transition region extends over some 40 K. The heat capacity is the mild function of M_n shown in *Figure 2*. Data are plotted for glasses at 250 K and liquids at 400 K. There is direct experimental information for most samples at these temperatures. The slope $\partial c_p / \partial (1/M_n)$ increases slightly with temperature in the glassy state but is constant for the liquid and any generalized equations must reflect this behaviour.

Glass temperatures were calculated as the points of intersection of enthalpy curves for the glassy and liquid states[2]. This procedure removes the effects of such factors as heating rate and sample mass and gives a T_g that characterizes the previous history. Heat capacities were integrated to give

$$H_g(T) = aT + 1/2bT^2 + P \qquad (1)$$

$$H_l(T) = AT + 1/2BT^2 + Q \qquad (2)$$

where P and Q are integration constants. Subtraction of equation (1), with $T = T_1$ from equation (2), with $T = T_2$, (T_1 and T_2 are in linear c_p–T regions, well away from the glass transition) gives $H_l(T_2) - H_g(T_1)$, an experimental quantity (the shaded area of *Figure 3*), so that Q–P may be calculated. The glass temperature then follows as the solution of the quadratic equation $H_g(T_g) = H_l(T_g)$ and results are shown in *Table 1*. The intermediate quantity $H_l(T_2) - H_g(T_1)$ is not given but may be calculated as

$$\int_{T_1}^{T_g} c_{pg} \, dT + \int_{T_g}^{T_2} c_{pl} \, dT$$

using the appropriate parameters from *Table 1* and any desired T_1, T_2.

DISCUSSION

Heat capacities

Generalized heat capacity equations were derived assuming additivity for the molar enthalpy H_m (ref. 6)

$$H_m = (n-2)H_\infty + 2H_e \qquad (3)$$

where n is the degree of polymerization, H_∞ the enthalpy

per mole of repeat units (MW 104.1) and H_e refers to a mole of end groups. The last term in equation (3) should formally be written $H_{e1} + H_{e2}$ to allow for the asymmetric n-butyl termination. Here they are replaced by $2H_e$ with an 'average' end group MW of 133.2. Differentiation and division by M_n gives the specific heat capacity

$$c_p = (nC_{p\infty}/M_n) + (2/M_n)(C_{pe} + C_{p\infty}) \qquad (4)$$

where capitals refer to molar quantities. At low MW the normal approximation $M_n/n \approx 104.1$ is invalid due to the terminal n-butyl group and the first term on the right hand side of equation (4) must be replaced by $c_{p\infty}(1 - 58.1/M)$ where $c_{p\infty} = C_{p\infty}/104.1$ and 58.1 is the excess end group contribution to M_n. Change from molar to specific heat units gives

$$c_p = c_{p\infty} + (c_{pe} - c_{p\infty})(266.4/M_n) \qquad (5)$$

and *Figure 2* shows that this equation holds down to pentamers, the minimum chain length studied. In fact for the liquid, the 'monomer', phenyl hexane, fits smoothly on the curve even though the low MW limit is, in principle, the n-butyl terminated dimer (equation 3). Both $c_{p\infty}$ and c_{pe} were assumed to be linear functions of temperature and $c_p - T - M_n$ data were fitted using a linear squares procedure to give (C_p in $Jg^{-1} deg^{-1}$, T in K)

$$c_{pg\infty} = -0.0785 + 4.35 \cdot 10^{-3} T \qquad (6)$$

$$c_{pl\infty} = 0.6771 + 3.12 \cdot 10^{-3} T \qquad (7)$$

$$c_{pge} = -0.0494 + 5.32 \cdot 10^{-3} T \qquad (8)$$

$$c_{ple} = 0.8707 + 3.09 \cdot 10^{-3} T \qquad (9)$$

$$\Delta c_{p\infty} = 0.7556 - 1.23 \cdot 10^{-3} T \qquad (10)$$

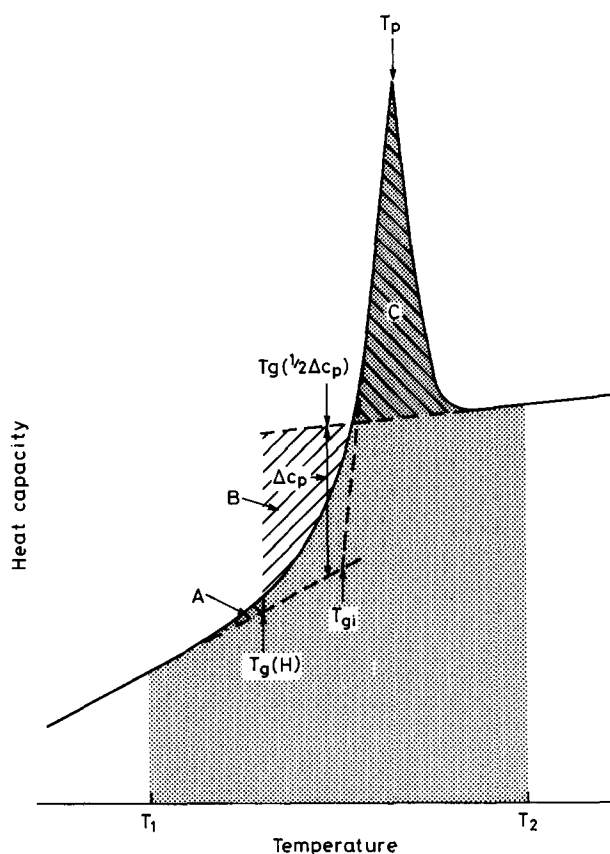$$\Delta c_{pe} = 0.9201 - 2.24 \cdot 10^{-3} T \qquad (11)$$

Figure 3 Constructions used for several definitions of T_g; see text for details

where $\Delta c_p = c_{pl} - c_{pg}$. For practical purposes $c_{p\infty}$ is the heat capacity of polymer with $M_n > 10^5$ and the figures from equations (6) (1.009 (250)) and (7) (1.925 J g^{-1} deg^{-1} at 400 K) are in excellent agreement with previous determinations using adiabatic calorimetry: 1.013 (anionic[7]), 1.015 (thermally polymerized[8]) at 250 and 1.918 J g^{-1} deg^{-1} at 400 K (ref. 8). This is well within the estimated $\pm 1\%$ overall accuracy of our measurements. There was no improvement in the fit if $c_{p\infty}$ and/or c_{pe} were allowed a quadratic dependence on temperature. Chang and Bestul[7] found a small temperature dependence of $\partial c_{pg}/\partial T$ which may be concealed in our smoothed data. These are marginally ($<1\%$) less than the adiabatic values at 200 (extrapolated) and 350 K. In the liquid state the temperature coefficient of $3.12 \cdot 10^{-3}$ J g^{-1} deg^{-2} extrapolates to give c_p within a few tenths of one per cent of the adiabatic result at 500 K (ref. 8).

Turning to the lower MW materials there are only minor (tenths of one per cent see, for example, *Figure 2*) differences between observed and 'calculated' (via equations (5)–(9)) heat capacities. These are 1–2% lower in the glassy state than those reported for thermally polymerized fractions with $M_n = 2300$ and 3650 (ref. 6) although this agreement may be fortuitous since results in reference 6 for the liquid state suggest that $c_{pl} < c_{pl\infty}$ which is the reverse of the behaviour shown in *Figure 2*.

Glass temperatures

Figure 4 shows the variation of T_g and T_g^{-1} with M_n^{-1} for glasses formed with $q = -5$ K min^{-1}. Experimental reproducibility is generally ± 1 K and deviations from the curves of *Figure 4* (which are discussed below) are normally within ± 2 K although this increases to $+4$ K in the region $M_n = 1000$–2000. This may reflect difficulties in determining M_n in this range: the negatively divergent point at $M_n = 2050$ represents a Pressure Chemical Company sample that has been characterized using different procedures (other, higher M_n, polymers from this manufacturer are indistinguishable from those shown in *Figure 4*). The curves of *Figure 4* are similar to those
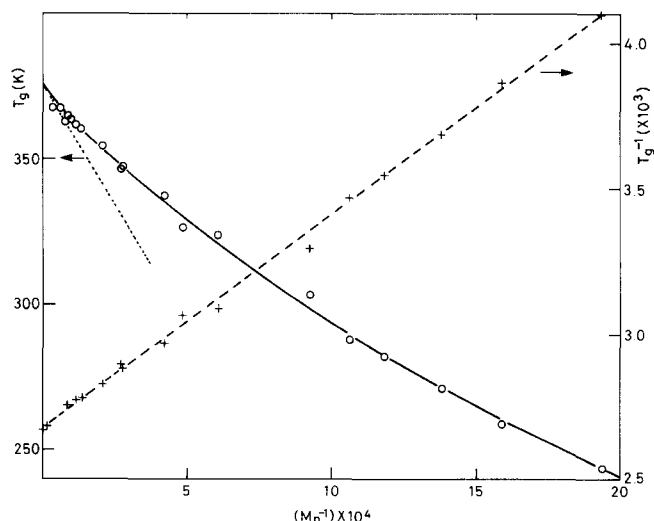
Table 2 The influence of cooling rate on T_g (K)

M_n	q (K min^{-1})	T_g (H)	T_{gi}	$T_g(\frac{1}{2}\Delta c_p)$
940	-0.3125	285.1	294.0	294.4
	-5	288.6	291.0	293.4
	-40	291.5	290.5	294.4
2 750 000	-0.3125	371.8	382.0	381.0
	-5	374.8	378.0	380.0
	-40	377.0	377.0	380.0

of other workers but precise comparison is difficult for both material and experimental reasons. The effect of thermal history has rarely been considered and there are no *a priori* reasons for assuming that the many processes that have been used to monitor T_g have relaxation times that lead to identical glass temperatures. Even for a given measurement there may be several 'definitions' of T_g and this is especially relevant for d.s.c.. For this technique the two most common definitions are the point of intersection of the low temperature curve with the line of maximum slope (T_{gi}, *Figure 3*) and that temperature where the heat capacity increment (Δc_p) has attained half its final value ($T(\frac{1}{2}\Delta c_p)$). $T_g(H)$, used in this paper, is equivalent to locating T_g so that areas $(A+C) = $ area B (*Figure 3*) and gives a thermodynamic quantity that refers to the initial glass and is independent of the d.s.c. heating rate. All three quantities are given in *Table 2* for the several glasses of *Figure 1*. Only $T_g(H)$ correctly shows the decrease of T_g with improved annealing (lower q values), $T_g(\frac{1}{2}\Delta c_p)$ is little affected and T_{gi} actually increases as q decreases. The last two constructions only give very approximate values for T_g with the approximation improving as the area C decreases, i.e. for quenched materials. The need for a careful specification of thermal history is particularly evident when T_g is only a few tens of degrees above ambient because in this region isothermal annealing is important. *Figure 5* shows curves for three freeze dried polymers after storage at room temperature for two years. The highest T_g material is relatively unaffected, the polymer with the lowest T_g has effectively come to equilibrium ($T_g = 294$ K) and the largest change is for the sample with a 'normal' T_g some 30 K above ambient which has been reduced by isothermal annealing to only 306 K. Conventional d.s.c. constructions fail to reflect these changes (*Figure 5*) which are important even for samples prepared only a few days prior to measurement because the processes involved show a logarithmic dependence on time.

The present results may be compared with earlier ones from this laboratory[9] which were derived from V–T data on very well annealed polymers ($q = -2.47$ K day$^{-1} \equiv -1.72 \cdot 10^{-3}$ K min^{-1}). *Table 1* shows that T_g decreases by about 2.5 and 2.9 K per decade decrease in q for $M \to \infty$ and 2050 respectively (the limiting M_n covered by reference 9). Using these figures the dilatometric T_g should increase to 375.7 and 327.4 K, respectively, for a $q = -5$ K min^{-1} glass, in good agreement with the present values of 375.2 and 326.5 K (in the latter case comparison is made with the experimental value shown in *Table 1* because of the uncertainty in M_n referred to above). This result implies that $T_g(V) \approx T_g(H)$ for this simple thermal treatment. (The qualification is required because differences are found under some circumstances[10].)
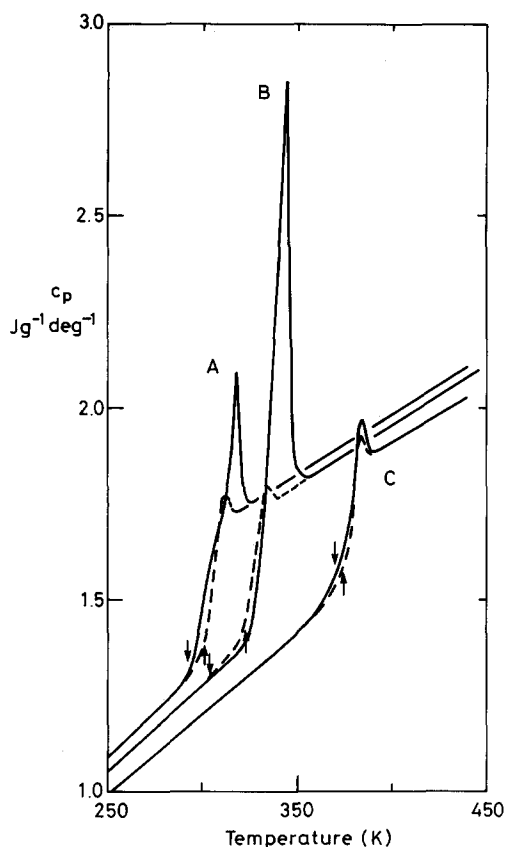

Figure 4 The effect of M_n on T_g. Glasses formed with $q = -5$ K min^{-1}. Points are experimental values (T_{go}) and the solid line is T_{gs}, *Table 1*, high M_n points are omitted. The dotted line represents equation (12) for $M_n > 20\,000$ with $T_{g\infty} = 375.0$ K and $A = 165\,000$; the broken line represents equation (13) for all data with $T_{g\infty} = 373.9$ K and $A' = 0.734$

Figure 5 Curves (——) showing how the glass transition region is influenced by annealing (2 years) at room temperature. The broken lines represent reruns after cooling at 40 K min^{-1}. Heating rate 20 K min^{-1}. $M_n = 1110$ (curve A), 1650 (curve B), and 68 000 (curve C). T_g is arrowed: $\downarrow$ (annealed), $\uparrow$ (rerun)

The generalization $\Delta\alpha \, T_g \approx 0.113$ ($\Delta\alpha = \alpha_l - \alpha_g$, $\alpha = (1/V(T_g))(\partial V/\partial T)$ where $V(T_g)$ is the specific volume at T_g) is a useful indication of free volume and Boyer[11] has suggested that there is a corresponding enthalpic expression $\Delta c_p T_g \approx 105 \text{ J g}^{-1}$. The present measurements cover a range of T_g from 240–375 K and so provide a useful model system that has consistent molecular parameters (the product is known to be influenced by chain stiffness, branching etc.). For the samples used here $\Delta c_p T_g$ varies linearly with M_n^{-1} from 110 ($M_n = \infty$) to 101 J g^{-1} ($M_n = 516$) so that the enthalpic approximation holds remarkably well for polystyrene.

MOLECULAR WEIGHT RELATIONSHIPS

Fox and Loshaek[12] have shown that both the Fox and Flory[13] and the Ueberreiter and Kanig[14] equations, (12) and (13), respectively

$$T_g = T_{g\infty} - A/M \tag{12}$$

$$1/T_g = 1/T_{g\infty} + A'/M \tag{13}$$

represent differing approximations to a more general T_g–M_n relationship (*Figure 4*). In particular equation (12) is only valid for high M_n although the meaning of 'high' may be obscured by experimental uncertainties. If, for example, data for the ranges $M_n \geq 10\,000$ or $\geq 20\,000$ are considered $T_g = 374.7$ or 375.0 K and $A = 128\,000$ or 165 000 respectively and it has been suggested[15] that A approaches 200 000 as $M \to \infty$. A simple average of all T_g for $M_n \geq 1\,000\,000$ is 375.2 K and this suggests that

slight curvature remains even above $M_n = 20\,000$. As the lower M_n limit is reduced, to give some sort of 'average' curve, both $T_{g\infty}$ and A decrease and the more familiar value of $A \sim 100\,000$ is found when data cover the range $M_n > 2000$.

It is clear from *Figure 4* that equation (13), with the parameters shown (which give $T_{ge} = 184.2$ K for the n-butyl terminated dimer) is a good approximation to the observed T_g–M_n data for this type of anionic polystyrene glass (characterized by $q = -5 \text{ K min}^{-1}$). The scale is not large enough to show the small, systematic deviations at high M_n. The smoothed data (T_{gs}) of *Table 1* are derived from large scale graphs of T_{go} against $\log M_n$ extrapolated to the average value at high M_n given above (375.2 K). In the MW range from 500–10 000 T_{gs} agrees with the values given by equation (13), and the parameters of *Figure 4*, to within a few tenths of a degree.

An approximate alternative form of equation (13) is obtained if M_n in equation (12) is replaced by $M_n + B$ (refs 12 and 16) (the constant B accounts for much of the curvature at low M_n). However, the performance of this modified equation with optimum values of $T_{g\infty} = 373.7$ K and $B = 246$ still falls short of that of equation (13) as shown by the lower value of $T_{g\infty}$. It should be noted that, for polystyrene at least, some of the criticism[16] of the physical reality of the Fox and Loschaek procedure[12] is removed for $B = 246$ as opposed to Fedors' values of 378 (ref. 16).

Thermodynamic and statistical mechanical theories that predict the variation of T_g with M_n have been given by Couchman[17–19] and by Gibbs and DiMarzio[20]. The thermodynamic approach assumes that a polymer of a given M_n can be represented by a mixture of chain end units (subscript e) and repeat units (subscript ∞) in the appropriate proportions. Equations for a particular thermodynamic property (entropy, S, enthalpy or specific volume) can be written in terms of contributions from end and repeat units plus mixing terms. The last are unknown but Couchman argued that the entropies of mixing are similar in the glassy and liquid states so that these terms effectively cancel at T_g where $S_g = S_l$. The final equation for an n-mer is

$$(n-2) \int_{T_{g\infty}}^{T_{gn}} \Delta C_{p\infty} \mathrm{d} \ln T + 2 \int_{T_{ge}}^{T_{gn}} \Delta C_{pe} \mathrm{d} \ln T = 0 \tag{14}$$

or, an alternative form in which the end group contributions are replaced by those of a particular oligomer of degree of polymerization m,

$$(n-m) \int_{T_{g\infty}}^{T_{gn}} \Delta C_{p\infty} \mathrm{d} \ln T + \int_{T_{gm}}^{T_{gn}} \Delta C_{pm} \mathrm{d} \ln T = 0 \tag{15}$$

In the above T_{ge}, T_{gm}, T_{gn}, and $T_{g\infty}$ are the glass temperatures of, respectively, an end unit, m- and n-mers, and the repeat unit with the properties of an infinite chain, ΔC_{pe}, ΔC_{pm} and $\Delta C_{p\infty}$ are molar heat capacity differences between the glassy and liquid states which may be calculated from the specific quantities given by equations (10) and (11). The assumptions made regarding the entropies of mixing have been criticized[21] and defended[22] but direct experimental evidence with which to test the theory has been lacking. In the original work it was assumed that the various ΔC_p were independent of temperature, ΔC_{pe} was derived from data of reference 6
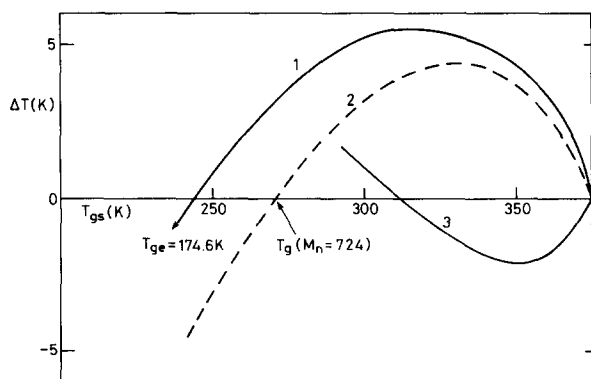
Figure 6 The difference ΔT between the calculated T_{gc} and smoothed T_{gs} (*Table 1*, $q = -5\,\mathrm{K\,min^{-1}}$) glass temperatures. T_{gc} calculated using the curves 1 and 2: Couchman theory using $T_{g\infty} = 375.2\,\mathrm{K}$, and the parameters shown above, in equations (14) (curve 1) or (15) (curve 2). Curve 3 T_{gc} calculated using the Gibbs–DiMarzio theory via Figure 8 of reference 26, and $T_{g\infty} = 375.2\,\mathrm{K}$

which, as discussed earlier, imply the unlikely condition c_{pl} (oligomer) $< c_{pl\infty}$.

Equations (14) and (15) are equivalent expressions: results for two sets of conditions are shown in *Figure 6* which gives T_{gc}, the calculated value of T_{gn} in equation (14) or (15), expressed as $\Delta T = T_{gc} - T_{gs}$, as a function of T_{gs} (*Table 1*). In curve 1 $T_{ge} = 174.6\,\mathrm{K}$ (this lies between $T_g(\text{styrene}) = 150\,\mathrm{K}$ (ref. 23) and $T_g(\text{distyrene}) = 195\,\mathrm{K}$ (refs 6 and 23) has been selected to give agreement in equation (14) at 244.0 K ($= T_g(M_n = 516)$) and in curve 2, using equation (15), $\Delta T = 0$ at 271.2 K ($= T_g(M_n = 724)$). T_{gc} is overestimated by, at most, about 5 K over a 130 K range so that equations (14) or (15) clearly have predictive value. The overestimate is reduced to only about 2 K if the M_n range is restricted to $T_g > 300\,\mathrm{K}$ (that is $M_n > 1000$) but no combination of 'reference' values can remove the curvature shown in *Figure 6* and the implication must be that a residual entropy of mixing exists and cannot be neglected. Possible confirmation of this comes from the behaviour of T_{gc} calculated from equivalent enthalpic equations, when the curvature is roughly double that shown in *Figure 6*, as would be expected for a relatively larger enthalpy of mixing term[22].

A direct experimental test of the Gibbs–DiMarzio statistical mechanical equations[20] is difficult and Kusy and Greenberg[24-26] have introduced a reduced variables technique that shows how several molecular parameters contribute to the variation of T_g with the degree of polymerization (n). For a given flex energy the greatest effects are cause by changes in N, the number of rotatable groups on one lattice site; the hole-to-flex energy ratio (r) can be varied within fairly wide limits without too much effect provided that, for any r, the free volume ratio is allowed to decrease with decrease in n. Figure 8 of reference 26 shows a reduced variables ($T_g/T_{g\infty}$ versus n^{-1}) plot for polystyrene. A wide range of experimental data can be accommodated with $N = 1.80$ and $r = 1.05$. The comparison of these calculated values (assuming $T_{g\infty} = 375.2\,\mathrm{K}$, i.e. for the $q = -5\,\mathrm{K\,min^{-1}}$ glass) with the data of *Table 1* is shown as curve 3 in *Figure 6*. For a given range of M_n results are similar to, but of opposite sign to, those obtained using equations (14) or (15). It should be emphasized that the deviations expressed as ΔT in *Figure 6* are systematic rather than random experimental effects. The enthalpic glass temperatures discussed

throughout this paper are thermodynamically defined quantities that, with increasing experimental sophistication, will be obtainable to fractions of a degree (even though the glassy region itself may cover tens of degrees) and on this scale it seems certain that there are deviations from both the thermodynamic and the statistical mechanical theories.

Whatever form of analytical equation is used for their description, the T_g–M_n curves of *Figure 4* appear smooth with no indication of the intersecting linear regions that have been suggested mark the onset of chain entanglements[27] or a change from oligomeric to polymeric behaviour[28].

THE EFFECT OF COOLING RATE

Earlier discussion has concentrated upon a specific glass (that with $q = -5\,\mathrm{K\,min^{-1}}$) which has been used to show how T_g is influenced by changes in M_n. This section will consider the effect of thermal history as reflected by changes in q. *Table 1* shows that T_g rises by nearly 6 K for an increase in q from -0.3125 to $-40\,\mathrm{K\,min^{-1}}$. A rise of 2–3 K per decade increase in q is common to many polymers[29] and, within the present limited 2.1 decade range in q, there is a linear relationship between T_g and $\log q$ for all the M_n studied (*Figure 7*). Since the overall change in T_g is only about 2%, this linear region could easily be part of a more general curve but, with this reservation, it is possible to derive an activation enthalpy (Δh) for the glass formation process. Moynihan[30,31] has shown that

$$\partial(\ln q)/\partial(1/T_g) = -\Delta h/R \tag{16}$$

where R is the gas constant, and *Figure 7* shows that this relationship is valid for the data of *Table 1*. The shape of the $\Delta h/R - M_n$ curve (*Figure 8*) reflects the T_g–M_n behaviour shown in *Figure 4* and equations similar to equations (12) and (13) may be used to describe the effect of M_n on $\Delta h/R$

$$10^{-3}\,\Delta h/R = 131 - (1.05 \times 10^5/M_n) \tag{17}$$

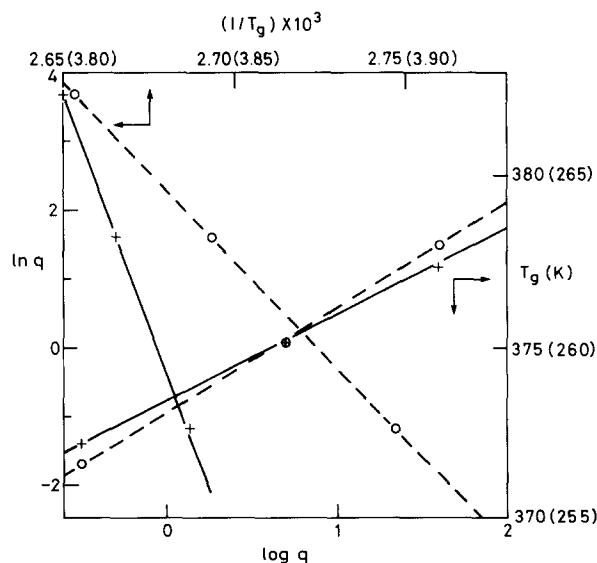$$1/(10^{-3} \times \Delta h/R) = 1/131 + 7.7/M_n \tag{18}$$

Figure 7 The effect of cooling rate (q, $\mathrm{K\,min^{-1}}$) on T_g. $M_n = 15\,000\,000$ (solid line), or 630 (broken lines and bracketed values of axes)
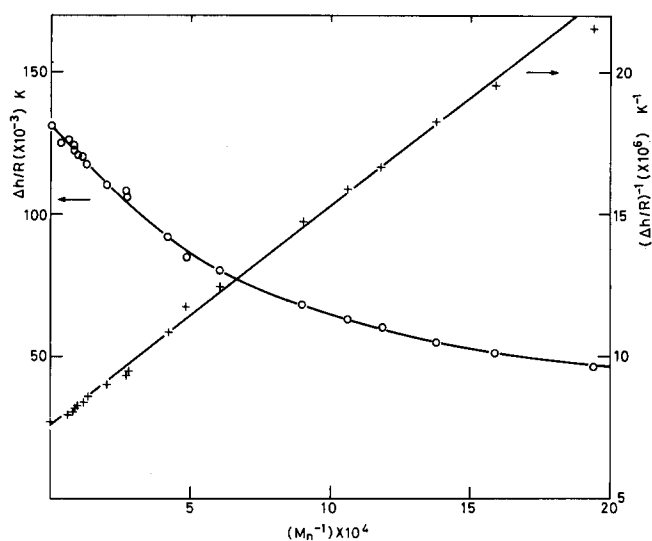
Figure 8 The influence of molecular weight on $\Delta h/R$. Points are calculated using the T_{gs} data of *Table 1*

Table 3 Activation enthalpies for polystyrene glasses

M_n	M_w/M_n	$10^{-3}\,\Delta h/R$ (K)	Reference
200 000	<1.06	175[a]	32
320 000	3.8	80	33, 34
2820	<1.1	80	35
31 000	<1.05	70	36
Various	various	107[b]	37
Various	all <1.1	131[b]	This work

[a] Calculated in reference 33
[b] Values for $M_n \to \infty$

The present results are compared with other data for polystyrene in *Table 3*. There is considerable scatter which cannot be explained by molecular weight effects since most data refer to regions where Δh is approaching its limiting value (equation 17). There is evidence from references 33 and 37 that a broadened molecular weight distribution reduces Δh but no evidence to support this has been found in this laboratory. The decrease in Δh with M_n shown in *Figure 8* is also demonstrated in reference 37 (albeit with an increased MW coefficient of 2.88×10^5) but contrary results are suggested[35,36] when an alternative, but equivalent, process (the variation of peak temperature, T_p, *Figure 3*, with heating rate for constant q) is used. It is clear from *Table 3* that great care is needed when deriving T_g so that its change with such variables as cooling rate and annealing time can be accurately defined.

The range of q used in this work is convenient for *in situ* d.s.c. experiments but a much wider span may be found in practice because most fabricated articles (and their precursor pellets) will have experienced some kind of quenching process equivalent to a cooling rate of several hundred degrees per minute. Unless thermal

history is carefully controlled, therefore, changes of ten or more degrees in T_g that are due solely to this effect may obscure details of the T_g-M_n curve. It is especially important to be aware of this if attempts are made to combine results from several authors to produce a comprehensive curve spanning a wide range of M_n.

ACKNOWLEDGEMENTS

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