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Structural recovery in isotropic and smectic glasses

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Abstract

The peak shift method has been used to derive parameters that characterise the glass transition of an isotropic and a smectic side chain liquid crystalline polymer. Results show more the universality of glass-formation behaviour rather than the influence of structural differences.

INTRODUCTION

The ageing of glasses is of both practical and theoretical importance. For many years one of the preferred methods of investigating the phenomenon has been to study dimensional changes using dilatometry or a related parameter such as the refractive index [1,2]. This is an ideal way to follow relatively slow changes under either isothermal conditions (after quenching, for example) or during a slow programmed change of temperature, perhaps some degrees per hour. More recently, it has become possible to investigate the behaviour of glasses formed under a much wider range of conditions by using differential scanning calorimetry (DSC). The very small samples required (of the order of milligrams) permit measurements to be made during heating and cooling at rates of up to perhaps one hundred degrees per minute. In DSC, the signal is related, not to the specific enthalpy (the thermodynamic analogue of the specific volume of dilatometry), but to its temperature derivative, the specific heat capacity c_p. DSC curves must therefore be integrated to observe the approach of a glass to an equilibrium state ("enthalpy relaxation") but against this minor inconvenience (with modern computing facilities) must be set the wealth of additional information that may be obtained from the DSC curve of the glass transition region. Depending on conditions, the heating curve, for example, may show a simple stepwise increase, as translational degrees of freedom are activated, or fine structure in the form of minima or, more

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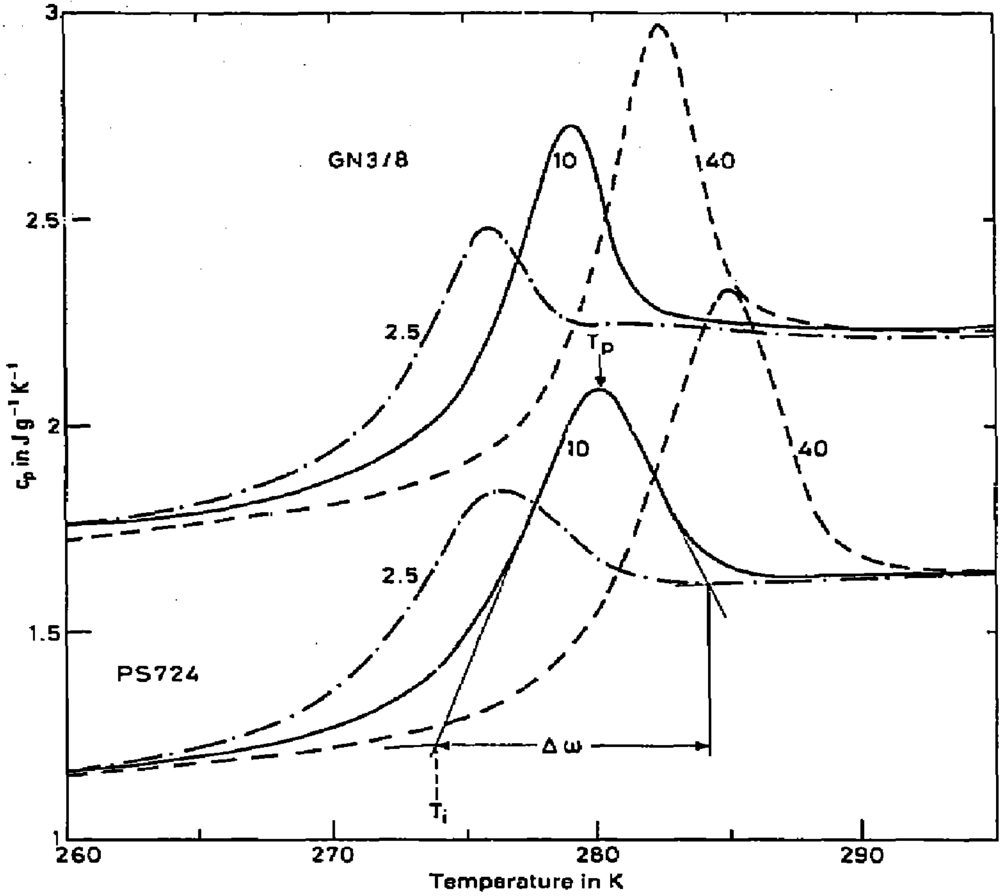


Fig. 1. The T_g region for a glass formed by cooling from the melt at 0.3125 K min^{-1} and then heated at the rates shown (K min^{-1}). PS724: lower curves. GN3/8: upper curves (displaced upwards by 0.5 J g^{-1} K^{-1}). The quantities T_i, T_p, and Δw are indicated.

frequently, peaks may be superimposed (Fig. 1). This additional structure is related both to the previous thermal and/or mechanical history and to the conditions of the DSC experiment itself. The study of these phenomena has been especially actively pursued by research groups associated with the names of Kovacs [3] and of Moynihan [4] and phenomenological models have been developed which satisfactorily reproduce the observed behaviour.

Development of the models of refs. 3 and 4 is based on similar basic assumptions and physical meanings have been ascribed to the several parameters. In particular, a partitioning factor x $(0 \leqslant x \leqslant 1)$ defines the relative contributions of temperature and structure (as reflected by the fictive temperature T_f) to the retardation time τ_0.

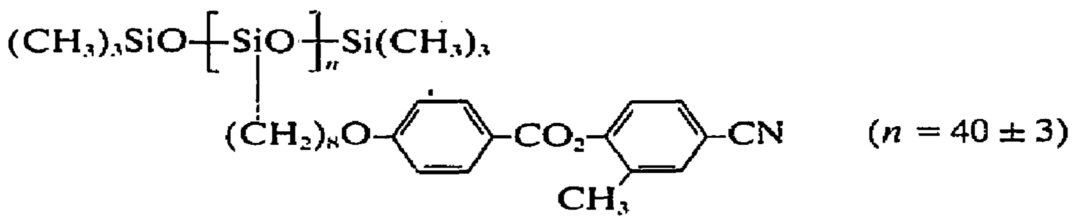
$$\tau_0 = A \exp[x\, \Delta h/RT + (1 - x)\, \Delta h/RT_f] \tag{1}$$

where A is a frequency factor, Δh an activation enthalpy and R is the gas constant [5]. Δh may be found from the variation of T_g (the limiting, low temperature value of T_f) with cooling rate [6] but x is normally obtained by a curve-fitting operating involving x, A and an additional parameter b that is inversely related to the breadth of the spectrum of relaxation times [7, 8]. It has been shown [9] how both Δh and x may also be obtained by a "peak shift" method that, because only one parameter at a time is determined, should be a more reliable approach than the alternative curve-fitting procedure. The method is so called because changes in the peak temperature T_p in the T_g region (Fig. 1) are followed as functions of a particular variable (cooling q_-, or heating, q_+, rate, annealing time and/or temperature) whilst the others are held constant.

In this paper the peak shift method is used to compare the behaviour of two very different glass-forming polymers (isotropic and liquid crystal) to see if there is evidence that any structural significance can be ascribed to Δh or x.

MATERIALS

The anionic polystyrene was an *n*-butyl-terminated oligomer (Polymer Laboratories) with a number average molar mass of 724 ($M_w/M_n < 1.10$, degree of polymerisation DP, 7). Thermodynamic properties have already been reported [11]. This particular M_n was chosen to give a T_g close to that of the smectic polymer (Structure 1).



Structure 1. GN3/8.

The preparation of the smectic side chain polysiloxane GN3/8 has been described [10, sample ID]. GPC analysis of the original poly(hydrogenmethylsiloxane) (Dow Corning DC1107) gave $M_w/M_n = 9950/3100 = 3.2$; NMR end group analysis gave $M_n = 2560$ (DP $= 40 \pm 3$); the same distribution and DP were assumed to characterise GN3/8. The glass transition was about 270 K (further discussion forms the body of this paper). On first heating GN3/8 in the DSC there were transitions at 320 and 364 K (enthalpy changes 1.3 and 3.1 J g^{-1}, respectively). The latter was the reversible smectic/isotropic transition. The event at about 320 K did not reappear and was probably due to partial crystallisation of the side groups; it was not observed in ref. 10 but the present sample had been stored at ambient for a much longer period.

CALORIMETRY

All measurements were made using a Perkin-Elmer DSC2 interfaced with an Olivetti microcomputer. The calorimeter was cooled using an Intracooler 2 to give a minimum convenient working temperature of 220 K. Measurements were always made in the specific heat mode [12] with a temperature calibration that allows for the finite size of the sample [13]. Because temperature plays such an important role in the final data analysis, it is discussed in more detail in a later section. Samples usually had a mass of about 10 mg, although for the two slowest heating rates (1.25 and 2.5 K min^{-1}) this was increased to 30 mg to give a reasonable signal size; some runs were also made on these larger samples at higher rates as part of the investigation into thermal lag.

The experimental procedure involved a series of controlled cooling and heating cycles that could also include a period of isothermal annealing. Cooling at different rates and/or isothermal annealing gives a series of glasses, the behaviour of which on subsequent heating is a function of the total thermal history (Figs. 1–3). Cooling rates q_- used in this work ranged from 0.3125–20 K min^{-1} and heating rates q_+ from 1.25–40 K min^{-1}. To save time, experiments at the slower rates covered the range from 240–300 K with the remainder extending from 220–340 K. It was essential to ensure that the sample was "stable" at 240 K on the time scale of the experiment [9]: samples were always reheated as soon as they came to equilibrium after cooling (2 min); no changes were observed in subsidiary experiments when this period was increased to 15 min; conversely, cooling was always started well above T_g ($\approx$270 K) to ensure that programmed conditions had been attained in the sample before T_g was reached. Isothermal annealing was used to produce a well-stabilised glass: samples were cooled at 20 K min^{-1} from 320 to 250 K and held there 64.25 h. (More rapid cooling gave an ill-defined product because the instrument lost control in the middle of the T_g region.)

RESULTS

The effect of q_+ on a particular glass (formed by cooling through T_g at $q_- = 0.3125$ K min^{-1}) is shown in Fig. 1 for both PS724 and GN3/8 and the reverse situation, varying q_- and constant q_+, is shown in Fig. 2. In all the examples of Figs. 1 and 2 the specific heat capacity in the low (c_{pg}, glass) and high (c_{pl}, liquid) temperature regions varied linearly with temperature and c_{pg} also appeared to be independent of thermal history. All curves therefore had common c_{pg} and c_{pl} regions, the effect of thermal treatment being limited to changes in the location and geometry of the transition region. Figures 1 and 2 show the heating portion of what have been called "intrinsic cycles" [14] for which the minimum temperature is low enough to prevent

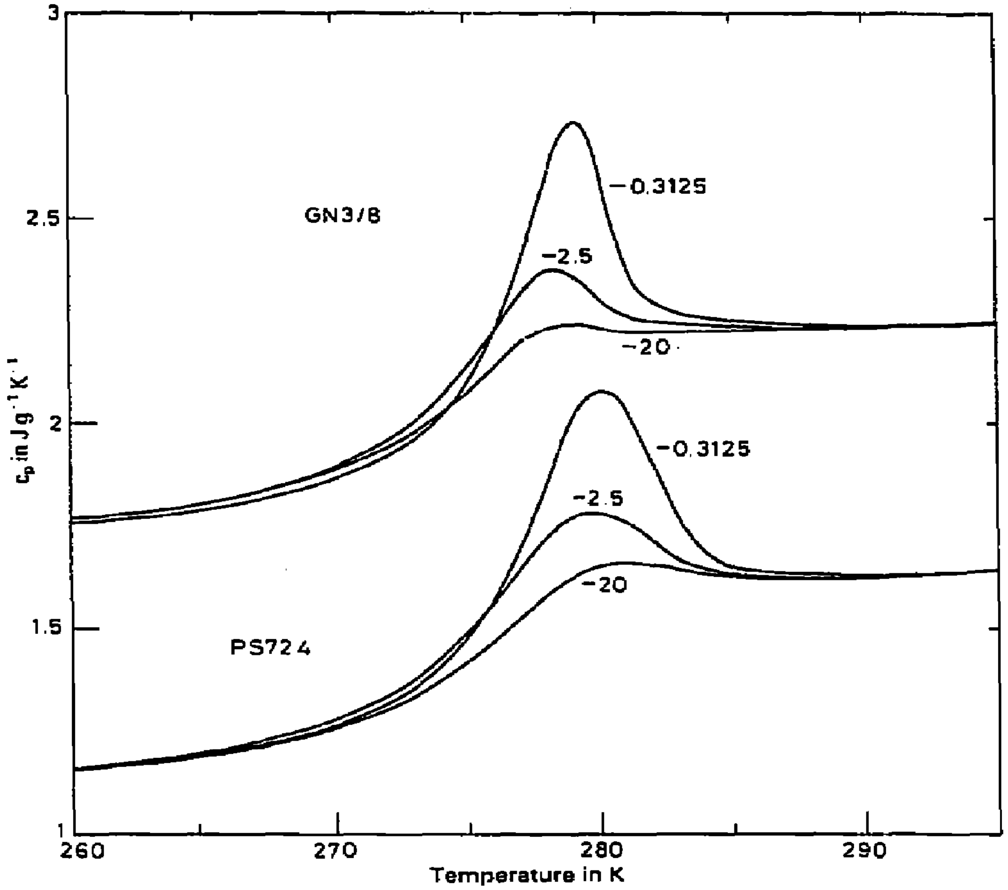


Fig. 2. As Fig. 1 but glasses formed by cooling through T_g at the rates (K min^{-1}) shown. All heating rates 10 K min^{-1}.

any isothermal relaxation, either deliberate or accidental. Figure 1 shows how T_i and T_p are defined and it is just possible to see (Fig. 2) how T_p passes through a minimum with q_- when q_+ = 10 K min^{-1}. The effect is clearer at higher q_+ but at the lowest heating rate T_p shows only an increase. This effect reflects the stability of the initial glass with respect to q_+; at high values most are stable but when q_+ is low there are structural changes on the time scale of the DSC experiment [15] and these are the cause of the differing behaviour.

A basic requirement of the peak shift method of determining x is a family of DSC curves, at various q_+, for a given well-stabilised, or enthalpy-relaxed, glass and these are shown in Fig. 3 for material annealed at 250 K for 64.25 h (in Figs. 1–3 the common c_{pg} and c_{pl} regions have been omitted).

Linear c_p–T regions were fitted by least squares procedures and smoothed values compared. All agreed to within ±1% even though individual values at the slowest heating rates (which gave only small "c_p" signals) varied by up to 3%. Data were combined to give the generalised

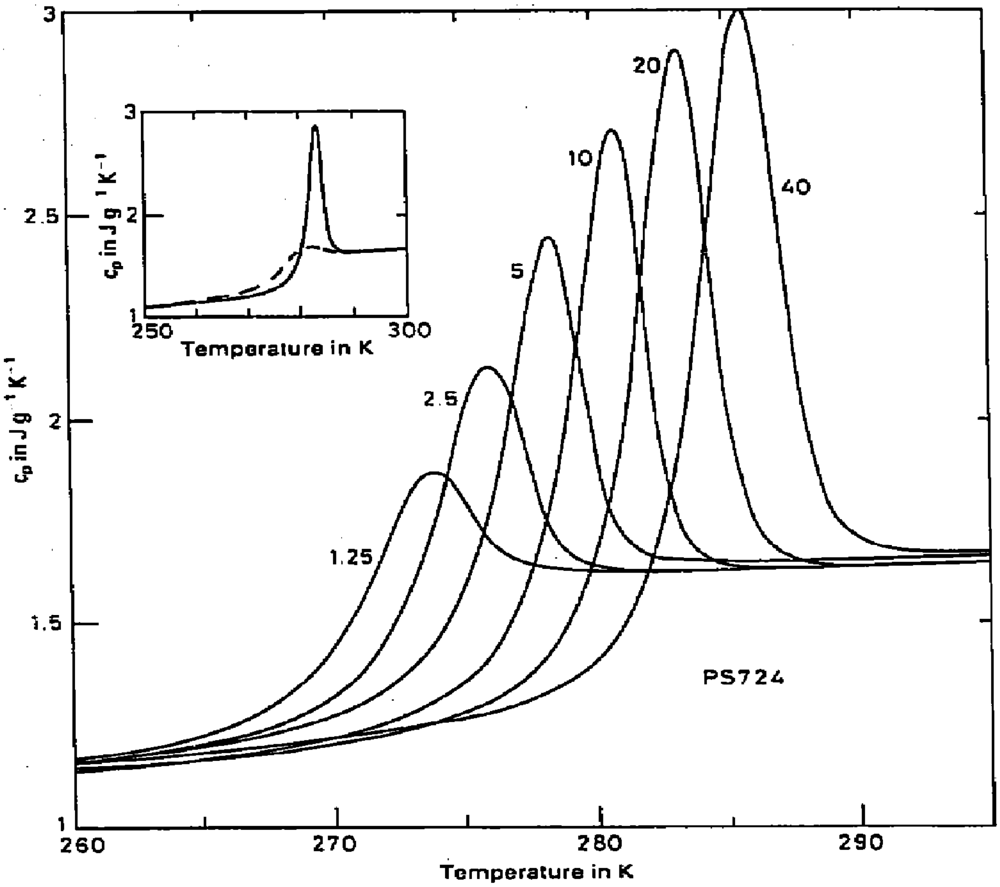


Fig. 3. The effect of heating rate (shown in K min^{-1}) on PS724 glass annealed for 64.25 h at 250 K. (Inset: annealed glass (q_+ = 20 K min^{-1}) showing also the glass after cooling and rerunning, all at 20 K min^{-1}.)

equations of Table 1 which lead to $c_{pg} = 1.109$ J g^{-1} K^{-1} (250 K) and $c_{pl} = 1.664$ J g^{-1} K^{-1} (300 K) for PS724 and these agree well with earlier reported values [11] of 1.114 and 1.674, respectively (note that table 1 of ref. 11 has numerical errors in the fourth column; for PS628/724/840 "A" should be 0.744/0.732/0.705 respectively).

TABLE 1

Specific heat capacity of PS724 and GN3/8 in J g^{-1} K^{-1}

Sample	Glass $c_{pg} = a + bT$		Liquid $c_{pl} = A + BT$	
	a	$b(\times 10^3)$	A	$B(\times 10^3)$
PS724	−0.174	5.13	0.740	3.08
GN3/8	0.011	4.75	1.237	1.67

TABLE 2

Glass transition temperatures in K after annealing at 250 K for 64.25 h

Sample	q_+/K min^{-1}					
	1.25	2.5	5	10	20	40
PS724	265.0	265.1	265.6	265.6	265.8	266.7
GN3/8	267.6	267.1	267.3	267.8	267.4	267.4

Conventional constructions that are supposed to give T_g from a DSC curve lead, in reality, to temperatures that are complex functions of the total thermal history (including q_+) of the sample. This is clearly incorrect if T_g is to be used to characterise a particular glass rather than the conditions of measurement. There is no reason to expect that different methods of measurement will give identical values of T_g; as a glass falls out of, or relaxes towards, equilibrium many processes are deactivated or activated and their detection is a function of the technique used, but this should still give consistent results. The point is emphasised when it is noted that well-annealed glasses appear to have higher T_g than quenched material (see inset, Fig. 3 where any characteristic point (T_i, T_p, etc.) on the unannealed curve lies below the corresponding point for the more stable material). The problem vanishes when the correct definition of T_g as the point of intersection of enthalpy curves for the glassy and liquid regions is taken [16]. When this procedure is adopted T_g becomes independent of q_+ and decreases for improved annealing conditions (low q_- and/or isothermal treatment). The accuracy of T_g did not appear to be significantly affected by the final heating rate: the glasses of Fig. 3 (which should have a common T_g) gave the values indicated in Table 2. Because of this, a simple average was taken (Fig. 4) for each of the several thermal histories used in this work. Figure 4 shows that for PS724 and GN3/8 T_g decreases by 3.1 and 2.3 K, respectively, per decade decrease in cooling rate. Each T_g shown in Fig. 4 is the mean of at least six values ($q_+ = 1.25, 2.5, \ldots, 40$ K min^{-1}) for which the usual uncertainty was a few tenths of a degree, but for which there were occasional larger deviations (e.g. 266.7 K for PS724, Table 2) of random sign; these were included in the averaging procedure.

DISCUSSION

The activation enthalpy for structural recovery Δh

This important parameter may be determined by two quite independent methods involving either the change of T_g with q_- or the shift in certain T_p with q_+.

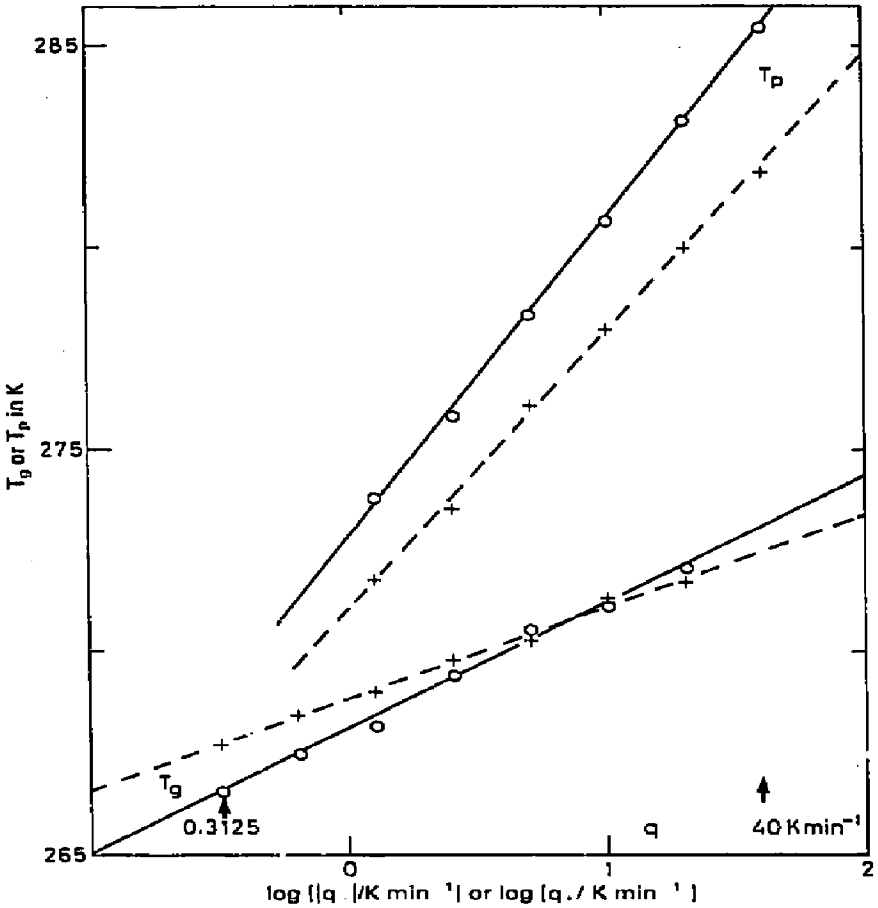


Fig. 4. Glass transition temperatures as a function of cooling rate (lower plots). The dependence of T_p (64.25 h anneal at 250 K) on heating rate (upper plots). PS724: full lines; GN3/8: broken lines.

Determination via T_g

It was shown some time ago [6] that $\mathrm{d}\ln|q_-|/\mathrm{d}T_g^{-1} = -\Delta h/R$ and when the data of Fig. 4 are fitted in this way $\Delta h = 440$ and 610 kJ mol^{-1} for PS724 and GN3/8, respectively. The former value compares well with 460 kJ mol^{-1} previously reported for this molar mass [11]: it should be emphasised that this refers to an oligomer; for conventional PS Δh may be more than twice as large [11].

The peak shift method

The alternative DSC approach to the derivation of Δh is through the slope $\mathrm{d}T_p/\mathrm{d}\ln q_+$ ($\equiv\theta^{-1}$) for intrinsic cycles with a constant ratio $|q_-|/q_+$ ($\equiv\rho$) [14]. Here T_p must refer to the "upper peak" found for an unstabilised glass (approximately when $\rho \geqslant 0.25$) and under these conditions $\Delta h/R = \theta T_g^2$.

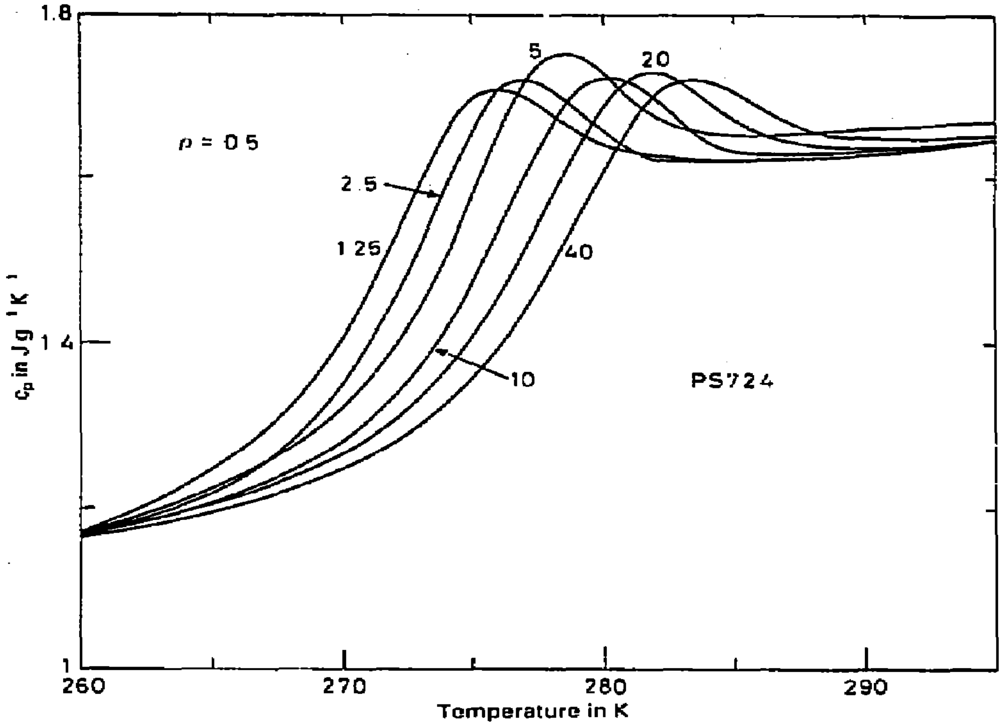


Fig. 5. The T_g region for PS724 glasses for which $|q_-|/q_+ = \rho = 0.5$. Heating rates are shown in K min^{-1}.

Graphs for $\rho = 0.5$ are shown in Fig. 5 and the corresponding peak temperatues are plotted in Fig. 6 which also gives the widths (Δw, Fig. 1) as a function of log q_+. The slight upturn in Δw was typical of all results for PS724 but for GN3/8 there was no discernible rate effect either for Δw or for the slope dT_p/d ln q_+. The latter is shown in Table 3 for a range of ρ and the resultant Δh (assuming $T_g \approx 270$ K, Fig. 4) appear at the foot of this table. For both materials the T_p-derived Δh values are only about 60% of the quantity obtained via T_g. One possible cause of this difference may be thermal lag within the sample itself. Any such effect will obviously increase with q_+ and the second value of θ^{-1} for PS724 given in Table 3 explores this possibility by restricting data to $q_+ \leqslant 10$ K min^{-1} for which thermal lag should, at least, be reduced; Table 3 shows that there is little change and this also holds for GN3/8. The restriction to $q_+ \leqslant 10$ K min^{-1} was based on the slight increase in Δw at higher rates (Fig. 6) which might imply that thermal lag was inadequately compensated at high q_+. This follows from a theoretical requirement [14] that, for a given ρ, a family of curves such as that in Fig. 5 should be superimposable by a simple shift. Although this can only be an approximation in a system for which the slopes of c_{pg} and c_{pl} differ, it formed the basis for the thermal lag correction when this method of determining Δh was first introduced [14]. Application of the procedure

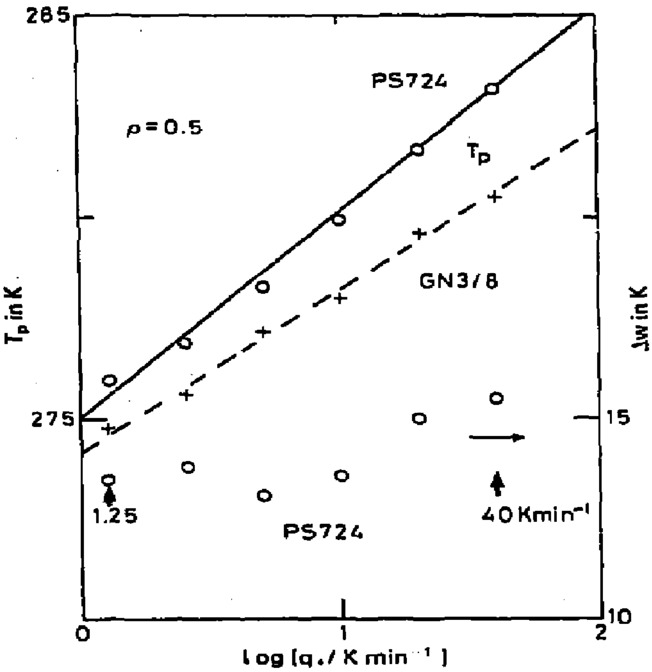


Fig. 6. T_p as a function of heating rate for $\rho = 0.5$ glasses for PS724 (upper curve) and GN3/8 (lower curve). Δw is shown for PS724.

of ref. 14 is somewhat artificial in the present case (for which a different type of correction has already been made, see below) but the calculations required can be made; again, the effect on θ^{-1} is slight.

The restrictions to $q_+ \leqslant 10$ K min^{-1} and the forcing of Δw to a constant value discussed above should have had only the minimal effects described

TABLE 3

θ^{-1} as a function of $\rho = |q_-|/q_+$

ρ	PS724		GN3/8
		$q_+ \leqslant 10$ K min^{-1}	
0.03125	2.52	–	1.59
0.0625	2.12	–	1.76
0.125	2.45	2.31	1.75
0.25	2.28	2.06	1.75
0.5	2.21	1.93	1.72
1	2.14	2.09	1.77
2	2.21	2.21	1.71
Average ($\rho \geqslant 0.25$)	2.21	2.07	1.74
Δh/kJ mol^{-1}	274	293	348
(via T_g)	(440)		(610)

because a correction for thermal lag has already been made: this is based on the rate of return to isothermal conditions at the end of a scanning experiment, a procedure that gives realistic changes in lag with sample mass and heating rate [13]. The correction is still, however, a single value that gives lag in the molten state whereas T_p refers to an ill-defined region where one "steady-state" (the glass) is changing to another (the liquid). It could be argued that some average for the two phases is more relevant for T_p itself, but it was shown earlier [17] that there is not a great difference between the two quantities: lag in the glass was 0.6 K greater than in the liquid for a 20 mg PS sample heated at 20 K min^{-1} (the dominant influence is the additional pan/glass interface (above T_g the liquid wets the pan) rather than changes in material properties). Subsidiary experiments on the 10 mg samples used here gave a difference in lag of 0.4 K. Uncertainties of 0.2 K have no significant effect on Δh.

These "phase" uncertainties probably only become important when very large samples are considered. The curves for 10 and 30 mg were superimposable at 1.25 and 2.5 K min^{-1}. At higher rates the heavier sample had increasingly broader curves so that at 40 K min^{-1} T_p was 0.8 K above that for the 10 mg sample. If simple proportionality is assumed, the "mass effect" implies that T_p should be reduced by 0.4 K for 10 mg at $q_+ = 40$ K min^{-1}, once again a negligible correction. If there were significant problems in the definition of temperature in the transition region itself it would be expected that these would be emphasised for those cases featuring the greatest discontinuity, well-annealed materials with large peaks (Fig. 3). It is clear from Fig. 4 that these give excellent linear T_p–ln q_+ curves. Here the definition of T_p is very clear and the apparent curvature in some of the results for $\rho \approx 1$ may be due to the greater difficulty in defining T_p for these curves.

If, as the above discussion implies, there are no major uncertainties in T_p, could the discrepancy in Δh be due to errors in the determination of T_g? This is found as the point of intersection of enthalpy curves from the glassy and liquid states. The transition region itself only influences the calculation through its (important) contribution to the total enthalpy change; the distribution with temperature does not matter provided all enthalpy is recorded. The calculation of T_g will be subject to a small error because a single, liquid-phase thermal lag was used whereas the "glassy state" extrapolation should have used the slightly higher lag discussed above. Differences should be emphasised at higher heating rates but Table 2 shows no obvious rate effects and T_g appears to characterise a particular glass to within a few tenths of a degree. At this stage, therefore, it appears to be impossible to reconcile the differences between Δh based on T_g or on T_p by appeal to experimental problems in determining one (or both) of these quantities. The two procedures should give equivalent results for Δh; there are no fundamental differences in their basic assumptions.

A common aspect is the higher value of Δh (however obtained) for GN3/8 relative to PS724 (the effect on T_g is clearly shown in Fig. 4), but differences, based on the sparse information that is available [11], are only what might be expected due to effects of molar mass rather than the structural contrasts between smectic and isotropic glasses. Similar results (to be published) have also been found for low molar mass organic glasses, both isotropic and liquid crystal.

The structural parameter x

This was obtained from the shift in peak temperature with heating rate for the glasses that had been well annealed by holding at 250 K for 64.25 h. The relevant equation is [9]

$$\theta \, \mathrm{d}T_p/\mathrm{d} \ln q_+ - 1 = F(x) \qquad (2)$$

where $F(x)$ is a function of x that is little influenced by the form assumed for the retardation time, it is essentially independent of both shape and breadth. The relationship between $F(x)$ and x is shown graphically in ref. 9. The relevant gradients (Fig. 4) are 3.41 and 2.95 for PS724 and BN3/8, respectively. Reduction of these to $F(x)$ requires a value for θ, and, as discussed above, this very much depends on the source, T_g or T_p. Using the data of Table 3 leads to the wide range for x given in Table 4. Irrespective of absolute values, the important conclusion is that there is little difference between the two materials.

CONCLUDING REMARKS

Full discussion of the significance of x as a structural parameter must await a better consensus of reported data. A major problem concerns the intermediate quantity Δh (or θ) for which there is unfortunately little agreement even for so well-investigated a polymer as polystyrene [11]. The ambiguities between T_g- and T_p-based data must be resolved before full advantage can be taken of the undoubted benefits of an independent (as opposed to global curve-fitting) method for the determination of x; only then can an assessment be made of the value of x for the characterisation of glasses.

TABLE 4

Structure parameter x

		PS724	GN3/8
Using θ:	via T_g	0.36	0.29
	via T_p	0.56	0.54

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