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Enthalpy relaxation in organic and inorganic glasses[1]

M.J. Richardson[a,*], M. Susa[b], K.C. Mills[a]

[a] *Division of Materials Metrology, National Physical Laboratory, Teddington, Middlesex TW11 0LW, UK*
[b] *Dept of Metallurgical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan*

Abstract

The effect of annealing (both by rate cooling and isothermally) on the thermodynamic properties of a sodium silicate glass in the vicinity of the glass transition has been measured. Changes in the glass transition and peak temperatures have been analysed to derive parameters that characterise the transition region.

Keywords: Annealing; Enthalpy; Glass; Relaxation; Transition

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1. Introduction

Most materials can be made to form a glass, either easily, as with conventional inorganic glasses or atactic polymers, or with difficulty, as is the case for metals. Many physical properties change dramatically over the glass transition region which therefore often represents the maximum or minimum service temperature of a material. Because of this, a glass transition temperature (T_g) is an important parameter for the characterisation of any material. A *single* glass temperature is really inadequate to define a *region* that may extend over several tens of degrees but is a convenient formalism, especially if the value varies in a meaningful way with the history of the sample. Here it is important to emphasise that *any* glass represents a metastable state that can relax towards some equilibrium condition–there is, therefore, no *unique* value for T_g, only a figure that reflects the history of the particular sample that is being examined. The variation of T_g with, say, cooling rate (q_-) is easily measured. Depending

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[*] Corresponding author; Now at: Polymer Research Centre, Dept. of Chemistry, Uni. of Surrey, Guildford, GU25XH, UK.

[1] Dedicated to Professor Hiroshi Suga.

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on the material, there may be a decrease in T_g of from 2 to 15 K per decade decrease in q_- for glasses formed by simple rate cooling (see, for example, Figs.1 and 4, below).

In principle, any property that changes in the vicinity of T_g can be used for its determination. In reality, there are often practical difficulties that prevent the widespread use of a particular property — many techniques, for example, require geometrically well-defined specimens that demand specialised fabrication procedures. Differential scanning calorimetry (DSC) has no such limitations — powdered, granular or film samples are all acceptable. The DSC output is related to the heat capacity of the sample which shows a step-wise increase on passing through the T_g region as translational degrees of freedom are activated. DSC has therefore become a favourite tool for studies of the behaviour of materials in the glass transition region [1–4]. "Behaviour" should be emphasised because a wide range of rate effects is observed owing to the comparable time scales for the experiment and for molecular motions. One result is that T_g *appears* to increase with DSC heating rate — just as with frequency, for example, when the experimental probe is a mechanical or dielectrical perturbation [5]. Although this gives valuable information about the kinetics of the transition, it contradicts the experience of many years of dilatometry by which annealing, however performed, inevitably decreases T_g. Fortunately, DSC is versatile enough to give the enthalpic analogue of the specific volume of dilatometry and it has been shown that this thermodynamic definition of T_g has equivalent properties [6].

Phenomenological theories of the glass transition have been developed in recent years and these can now predict the often complex DSC behaviour that is associated with particular thermal histories [7–9]. The latter are often also associated with changes in important end-use properties such as impact strength; tests for this are notoriously unreliable and their replacement, at least for routine testing, by simple DSC work is an attractive proposition. Also attractive is the potential to model changes to the DSC curves caused by time/temperature/stress regimes on the sample and their correlation with end-use properties.

The working parameters required by phenomenological theories are obtained by various curve-fitting procedures. A basic quantity is the activation enthalpy (Δh^*) which is obtained [10] from the change in either the glass temperature (T_{gH}) with q_- or the peak temperature (T_p, Fig.1) with heating rate (q_+) for samples having a constant ratio (ρ) of cooling to heating rate ($\rho = |q_-|/q_+$)

$$\mathrm{d}\ln|q_-|/\mathrm{d}(1/T_{gH}) = [\mathrm{d}\ln q_+/\mathrm{d}(1/T_p)]_\rho = -\Delta h^*/R \qquad (1)$$

where T_{gH} is equivalent to the limiting, low-temperature fictive temperature (T_f') and R is the gas constant. Any glass is always attempting to attain the lower energy equilibrium condition that characterises a particular state and a basic quantity here is the relaxation time τ. It is found that τ depends on both temperature and some structural parameter that is conveniently represented by the fictive temperature (T_f). The partitioning of the two effects may be represented by [11]

$$\tau = \tau_o \exp[x\Delta h^*/RT + (1-x)\Delta h^*/RT_f] \qquad (2)$$

where x ($0 \leqslant x \leqslant 1$) is a structural or non-linearity parameter. The three parameters, Δh^*, τ_o, and x, plus an additional one (β), which characterises the distribution of relaxation times [12], can, in principle, give a complete description of rate effects in the T_g region. There are problems. Although Δh^* can be derived from either of the expressions of Eq. (1), different results are found [13]. The remaining parameters are generally obtained simultaneously via a curve-fitting procedure [14] but an alternative approach [15] permits individual determination and this is especially useful if x can be shown to be an inherent material property. Earlier work [13] that addressed this problem focussed on two different low molar mass polymeric glass-formers (one a polystyrene oligomer, the other having liquid crystal-forming side chains) with $T_g \simeq 270$ K. In this paper, the behaviour of those materials is compared with that of a sodium silicate glass having a much higher glass transition region ($\simeq 750$ K).

2. Materials

The $Na_2O.2SiO_2$ was prepared by heating stoichiometric amounts of sodium carbonate and silica to 1620 K in a muffle furnace and quenching the product on to a stainless steel disc.

Well-annealed glasses were produced by oven-heating a batch of samples (each about 30 mg and contained in platinum pans) to 860 K, well above the glass transition region.The batch was then removed and placed directly in another oven pre-set at the annealing temperature of 680 K where samples were kept for 96 h before removal and air-quenching to room temperature. Rate-cooling experiments were carried out in the DSC with particular care being taken to ensure that cooling was started well above T_g: this ensured that the programmed value of q_- had been attained before the T_g region was reached; for the highest value of $q = 80\,\text{K min}^{-1}$ this required a starting temperature of 880 K.

3. Calorimetry

Measurements were made using a Perkin-Elmer DSC2 interfaced with an Olivetti microcomputer using data processing procedures that have been described earlier [16]. The calorimeter was cooled by an ice/water bath. Temperature calibration was based on an isothermal step-wise procedure [16] using indium, tin, lead, zinc and aluminium. All metals except aluminium were melted in aluminium pans; aluminium was contained between 0.1 mm sapphire discs in a platinum pan. Similar treatment to the zinc sample gave only a minor (< 0.1 K) increase in the apparent isothermal melting point, and there was no change when aluminium was melted in alumina pans. The resultant calibration curve was almost linear with temperature and was used with a thermal lag term [17] to correct the apparent temperature at any q_+. All DSC experiments were carried out in the specific heat mode using alumina as the calibrant.

4. Results

The effect of prior cooling rate on samples heated through the T_g region at 20 K min^{-1} is shown in Fig.1 which also defines the quantities T_i and T_p for the curve with

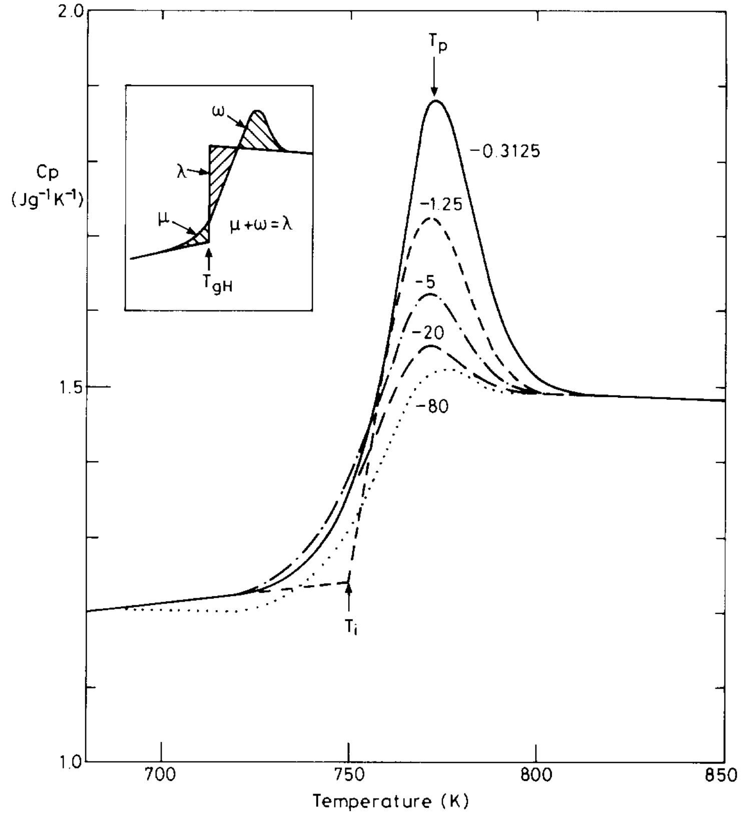

Fig. 1. The effect of previous cooling rate (shown in K min^{-1}) on the heat capacity of sodium silicate heated through the glass transition region at 20 K min^{-1}. T_i and T_p are shown for the sample cooled at 0.3125 K min^{-1}. Inset shows the geometric construction that defines T_{gH}.

$q_- = 0.3125$ K min^{-1}. It is clear that the most unstable glass, for $q_- = 80$ K min^{-1}, anneals on heating as shown by the downward displacement of the curve for this glass above about 680 K. This is in accord with theoretical predictions [7] as is the locus of T_p with q_-[18], an initial decrease followed by a progressive increase.

Curves showing the influence of heating rate on T_p for samples with $\rho = 1$ and after annealing for 96 h at 680 K are given in Figs. 2 and 3, respectively. The numerous data sets gave a clear definition of the specific heat capacity in the glassy (subscript g) and liquid (subscript l) states. Both c_{pg} and c_{pl} varied linearly with temperature over the ranges covered

$$c_{pg} = 0.803 + 5.8 \times 10^{-4}T \quad \mathrm{J\,g^{-1}\,K^{-1}} \quad \text{(valid 600–660 K)} \tag{3}$$

$$c_{pl} = 1.586 - 1.2 \times 10^{-4}T \quad \mathrm{J\,g^{-1}\,K^{-1}} \quad \text{(valid 820–880 K)} \tag{4}$$

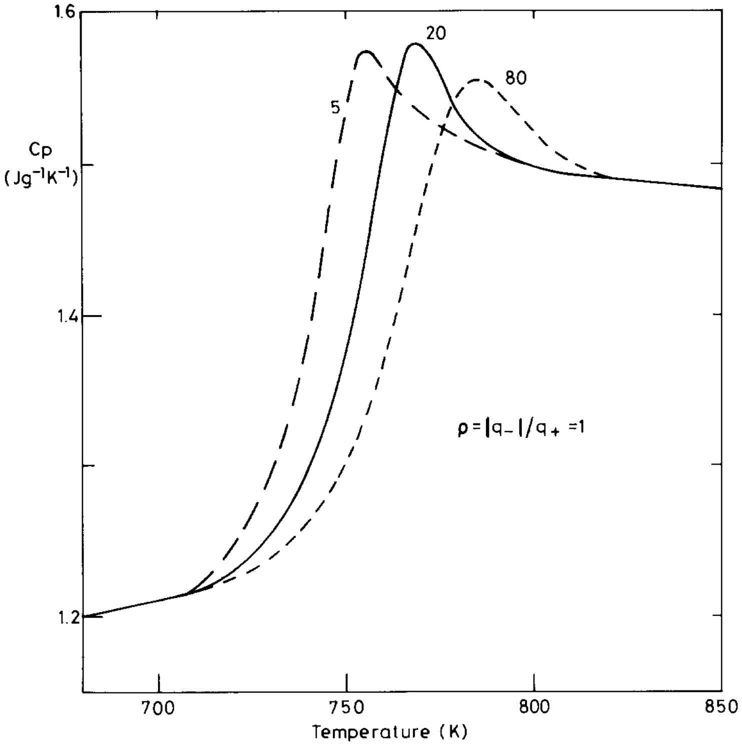

Fig. 2. Heat capacity curves for sodium silicate (previously cooled through T_g at the same rate as subsequently heated) heated at the rates shown (K min^{-1}).

The temperature coefficient in the liquid state is close to zero but shorter runs between 820 and 880 K, which were made in both heating and cooling specifically to investigate this point, always gave a negative coefficient similar to that of Eq. (4) (shorter runs are more accurate, being less influenced by baseline errors [16]). Eqs. (3) and (4) are average values from some 30 runs with maximum deviations in all cases of less than 2%. This is double the range reported for data at lower temperatures [13]; it does not include c_p data generated at $q_+ = 1.25$ and 2.5 K min^{-1} which gave small signals that were only suitable for the definition of T_p.

Enthalpic glass transition temperatures, calculated as the point of intersection of enthalpy curves for the glassy and liquid states [6], were derived from Eqs. (3) and (4) and from the overall enthalpy change from the glass to the liquid. They are shown in Fig. 4 which also shows T_p and , for comparison, similar data for a low molar mass (724) polystyrene [13]. All the samples annealed for 96 h at 680 K should have the same value of T_{gH}; in fact values ranged from 699 to 705 K with a mean of 702 K. The same span of 6 K also covered all ten values of T_{gH} (mean,739.5 K) found for glasses formed by cooling at 20 K min^{-1} with heating rates from 5 to 40 K min^{-1} (T_{gH} was randomly distributed about q_+). Polymeric glasses with T_g in the range 300–500 K usually show

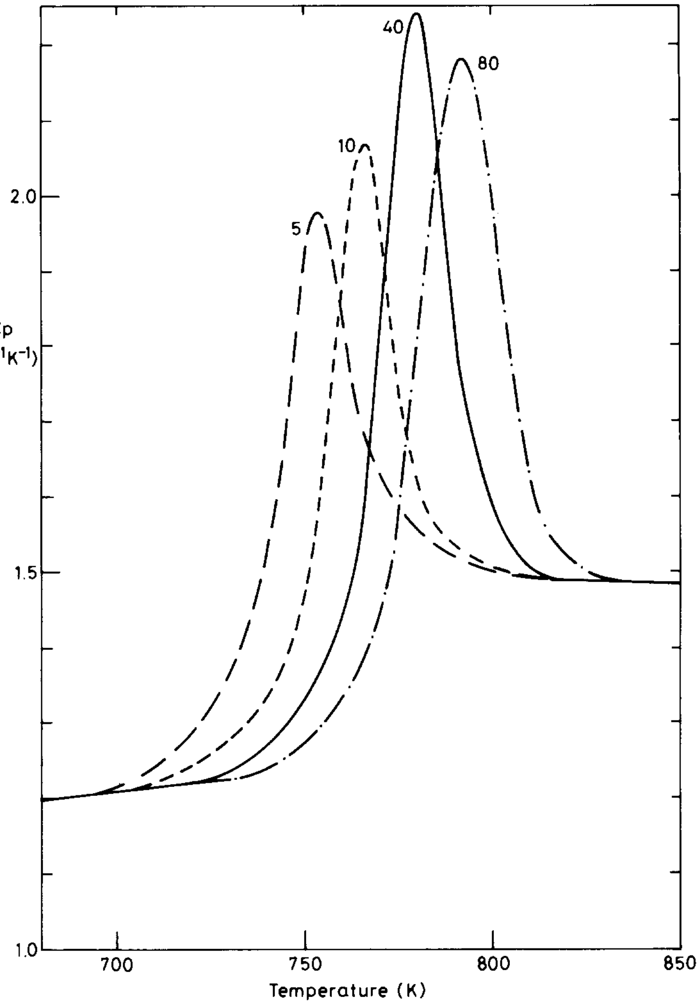

Fig. 3. The effect of heating rate (shown in K $\min^{-1}$) on DSC heat capacity curves for well-annealed (96 h at 680 K) sodium silicate.

a reproducibility of ± 1 K in T_{gH} [13] and the wider range found here reflects the greater difficulties associated with high-temperature DSC work. Uncertainties of the order of several degrees in T_{gH} should lead to considerable doubt in any quantity based on changes in T_{gH} with q_-, in particular, Eq. (1). Two observations reduce the problem: (i) the effect of q_- on T_{gH} for $Na_2O.2SiO_2$ scales, very crudely, with temperature relative to earlier work [13], and (ii) variations in T_{gH} occur from day to day rather than within a sequence of experiments on an undisturbed sample.For the last, there were similar changes of T_{gH} with q_-, but also overall variations of ± 3 K in T_{gH}. For example, three sets of data, for q_- varying from 1 to 80 K $\min^{-1}$, gave $\Delta h^* / R = (102, 88, 105) \times 10^3$ K

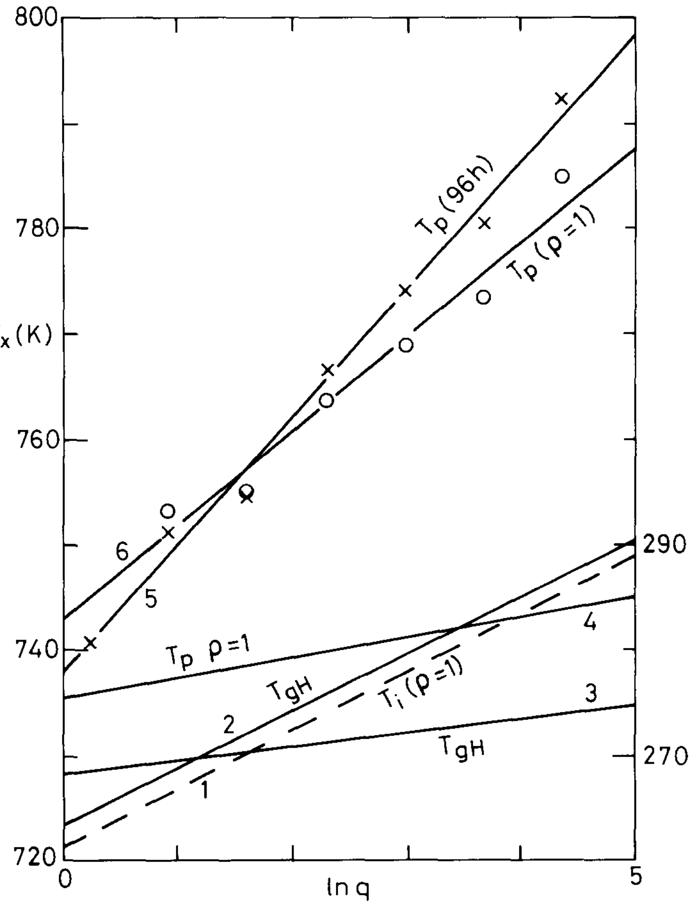

Fig. 4. Characteristic temperatures T_x (see text) for sodium silicate (left-hand ordinate, curves 1, 2, 5, 6) and low (724) molar mass polystrene (right-hand ordinate, curves 3, 4) as a function of cooling (T_{gH}) or heating rate (remainder).

with corresponding $T_{gH}(q_- = 20\ \mathrm{K min}^{-1})$ of 736.3, 738.4, 741.5 K, but no point in a particular set deviated by more than 1.5 K from its individual $\ln|q_-|$ vs. $1/T_{gH}$ relationship.

5. Discussion

5.1 Activation enthalpy Δh^*

5.1.1. Δh^* *via* T_{gH}

The derivation of T_{gH} [6] and, from this, of Δh^* via Eq. (1), is straightforward. The formal construction of enthalpy–temperature curves is not required. This could, in fact, be counter-productive in the sense that the slopes, i.e. c_{pg}, c_{pl}, of the glassy and liquid portions differ by only some 25% (Eqs. (3), (4)) and the necessary extrapolations, from outside the T_g region to $H(\text{glass}, T_g) = H(\text{liquid}, T_g)$, are difficult to make by eye with any precision. The computational procedure of Ref.[6] requires no such subjective judgement. It is equivalent to locating T_g so that the areas $\mu + \omega = \lambda$ (inset, Fig. 1); this last approach [19] is direct but background curvature for the DSC trace should be minimised. The mean value, $\Delta h^* = 820 \pm 70$ kJ mol^{-1}, is in line with the generally large values reported for this parameter[20]. All experiments from which Δh^* was derived were based on a heating rate of 20 K min^{-1}, a value that was chosen to optimise heat capacities (reproducibility ± 2% at these temperatures). T_{gH} is a quantity that characterises a particular *glass* (not the transition *region*) and should be independent of q_+: in the present case, "particular glasses" were formed by varying q_- and it was noted above that T_{gH} ($q_- = 20$ K min^{-1}) was indeed independent of q_+. T_{gH} is, therefore, a true materials parameter (albeit a function of q_-) and a worthy candidate for the description "glass temperature". By contrast, the observed behaviour in the T_g region, in a DSC curve just as in any other rate experiment, is dominated by kinetic effects and any point in this region that purports to be "T_g" must be heavily qualified. It is, however, possible to utilise some of these "T_g" values in alternative methods for deriving Δh^* and these are now considered.

5.1.2. Δh^* *via* T_i, T_p

It was shown in Ref. [1] that *any* characteristic temperature T_x (x = onset, inflection, peak, etc.) from the T_g region of a family of DSC curves having a constant value of ρ could be used to derive an activation enthalpy (Eq. (1), T_p is shown). More recently Hutchinson and Ruddy [15] have discussed a "peak shift" method from which both Δh^* and x (Eq. (2)) may be obtained. In Ref. [15] the prime requirement for Δh^* is, again, the change of T_p with q_+ as given by Eq. (1). Ideally, T_p could be replaced by T_i because c_p–T curves having a given value of ρ should be superimposable by a simple shift along the temperature axis, i.e. all should have the same shape [1,21]. Although this has been shown to be a good approximation (see below) for B_2O_3 [1] and for some organic polymers [13], it is certainly not true here (Fig. 2). In Ref. [13], for example, $T_p - T_i$ for the polystyrene oligomer was 9.3 ± 0.3 K, and specific values varied quite randomly for heating rates from 1.25 to 20 K min^{-1}; in the present work, however, $T_p - T_i$ increases linearly with q_+ (given in brackets) from 25.0 K (2.5 K min^{-1}) to 33.0 K (40 K min^{-1}). The resultant T_i or T_p vs. $\log q_+$ curves, although both linear, therefore have different slops (Fig. 4) and there is ambiguity in the derived values of Δh^*. It is tempting to accept the value obtained from the "onset" temperature T_i because this is close to that from T_{gH} data (810 and 820 kJ mol^{-1} respectively) and ascribe the lower "T_p" value (560 kJ mol^{-1}) to thermal lag in the transition region (because T_p/ appears to be artificially high, the effect of q_+ is exaggerated and a lower *apparent* value of Δh^* is obtained). A similar effect was, indeed, used to correct for thermal lag [21] by forcing all T_g regions to cover the same temperature span but there are fundamental differences from the present work. Ref. [21] was a development that was intended to allow for the thermal effect of a finite sample mass which revealed itself as curvature in the uncorrected T_p vs. $\ln q_+$ relationship (in Ref. [21] the conventional indium melting correction had been made but this only gives the temperature at the sample *face* in contact with the pan and makes no allowance for sample thickness). In the present work, allowance has been made [17] for sample thermal lag and it is noteworthy that there is no curvature in either of the T_i or T_p curves ($\rho = 1$) of Fig. 4. In fact, specific tests show little difference between thermal lag in the glassy and liquid phases. There is still a perturbation in steady state conditions on passing from the glassy to the liquid state and if this is magnified by a large "annealing" peak there could still be significant lag. However, for the condition $\rho = 1$, the "peak" is of minimal size and even when much larger (Figs. 2 and 3, respectively) there is still a linear change of T_p with ln q_+ (Fig. 4), whereas the effects of thermal lag would be expected to give positive curvature at high q_+ (as observed in Ref. [21]).

It appears that, although the qualitative behaviour of the whole family of glasses is similar, there are significant detail differences. One obvious point concerns the "superimposability" of curves for $\rho =$ constant. To a very good approximation, c_{pg} is independent of prior history and all c_p vs. T curves have common glassy and liquid regions. Because there is a finite slope in both these regions, it is never possible to superimpose in the T_g region by any kind of shift; this can only be done when $\mathrm{d}c_p/\mathrm{d}T = 0$. Even in Ref. [13], although $T_p - T_i =$ constant, it was not possible to shift curves to a common T_g region.

5.2. *The non-linearity parameter* x

The most convenient of the "direct" methods for the determination of x uses the change of peak temperature with heating rate for a well-annealed glass [15]. This is linked to x via a function $F(x)$ that has been theoretically related to x [22] by

$$(\Delta h^*/RT_g^2)(\mathrm{d}T_p/\mathrm{d}\ln q_+)_{q\ ,T_1,\delta_H} - 1 = F(x) \tag{5}$$

where q_-, T_1 and δ_H emphasise that all T_p refer to a glass that has been cooled at a constant rate q_- (here a quench) to a temperature T_1 (680 K) and held there for a fixed, but lengthy, period (96–h) to allow the glass to become well stablished. The enthalpy decrease $\delta_H = 10.4\ \mathrm{J\,g^{-1}}$ may be calculated from the T_{gH} values given earlier and Eqs. (3) and (4): typical "limiting" values for organic glasses are perhaps 3–4 J g^{-1} [15] and the much greater figure here is due to the larger changes in T_g on annealing.

Fig. 4 shows $\mathrm{d}T_p/\mathrm{d}\ln q_+$. As already emphasised, the relationship is linear and the slope is 11.96. For this sample $T_{gH} = 702$ K and $F(x) = 1.38$ or 0.63 for $\Delta h^*/R$ derived, as discussed above, from T_{gH}(or T_i) or T_p, respectively. The corresponding values of x (obtained using the graphical relationship between $F(x)$ and x given in Ref. [15]) are 0.37 and 0.58. This extreme sensitivity to the method of data treatment must raise doubts as to the value of x as a "structural" parameter for the characterisation of a glass. There is evidence from curve-fitting procedures that the parameters of Eq. (2) change systematically with thermal history [23]. Indeed, it is possible to derive an alternative form of Eq. (2), based on the Adam–Gibbs expression for τ_o [9], which suggests that x may be related to the limiting fictive temperature. Certainly, based on Ref. [13] and the present work, there are difficulties in accepting that x has a unique structural significance. This being said, it should be noted that very similar values of x were found for the polystyrene oligomer, the side-chain liquid crystal polymer and the present sodium silicate (in order: $x = 0.36, 0.29, 0.37$ based on Δh^* via T_{gH} or 0.56, 0.54, 0.58 via T_{p}). It has been suggested [9] that x is related to the "fragility" [24] of the glass. "Fragility" reflects changes that occur on passing from the glass to the liquid; fragile glasses experience major breakdowns in structure in the T_{g} region (shown, for example, by a large Δc_{p} step and low x), whereas a strong glass such as silica is little affected. Both the organic glasses of Ref. [13] have a reduced ($c_{pr} = c_{pl}/c_{pg}$) heat capacity of $\approx$ 1.3 at T_{g}; for $Na_2O.2SiO_2$, c_{pr} is 1.2. These numbers suggest glasses of intermediate strength and this supports the data for x that are based on Δh^* from T_{gH} rather than from T_{p}: values of x approaching 0.5 are incompatible with a glass of only modest "strength".

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