

# Glass transition and thermodynamic state of densified polymeric glasses\*

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Differential scanning calorimetry (d.s.c.) and specific volume,  $V$ , measurements have been made on polystyrene glasses formed by cooling from the melt under pressure. Conventional glass temperatures,  $T_g(H)$  and  $T_g(V)$ , defined by the points of intersection of enthalpy,  $H$ , or  $V$  curves for the glass and liquid agree well for one atmosphere glasses but show very different behaviour if the glass has been formed under pressure. This is due to the inability of the high pressure glasses to attain a suitable liquid conformation at atmospheric pressure. The thermodynamic state of densified glasses is discussed.

## INTRODUCTION

The vitrification of common amorphous polymers by cooling from the melt under high hydrostatic pressure has been shown<sup>1-3</sup> to give glasses with densities that are higher than those formed by comparable cooling under atmospheric pressure. Typically the density increase is of the order of 1% per 100 MN/m<sup>2</sup>. Previous work on such densified glasses has shown complex pressure–volume–temperature<sup>4</sup>, specific heat ( $C_p$ )–temperature<sup>5-8</sup> and enthalpy–densification pressure<sup>5,9,10</sup> relationships.

Since quenched glasses anneal to denser states<sup>11</sup> it could be argued that densified glasses represent a closer approach to equilibrium but in fact the materials relax *towards* normal density values as the glass temperature,  $T_g$ , is approached<sup>6,10</sup>. This complex behaviour leads to problems in determining  $T_g$ . Two methods (specific volume and enthalpy) which give almost identical  $T_g$  values for one atmosphere glasses<sup>12</sup> give contradictory results when applied to densified material. The present study was undertaken to resolve these apparent inconsistencies. Thermal and volumetric properties of glasses densified under pressures of up to 350 MN/m<sup>2</sup> were investigated by differential scanning calorimetry, d.s.c. and dilatometry, care being taken to use similar conditions in the parallel experiments to allow a direct comparison of experimental results.

## EXPERIMENTAL

### Materials and densification procedure

Measurements were made on polystyrene, both anionically (Pressure Chemical Co.,  $M_n = 20\,400$ ,  $110\,000$ ,  $2\,000\,000$ ) and thermally polymerized (BDH,  $M_n = 150\,000$ ).

Polymer was first moulded into  $10 \times 10 \times 60$  mm bars from which rods 3.6 mm diameter  $\times$  20 mm long were machined; these had a concentric hole, 1.55 mm diameter  $\times$  10 mm long at one end. The rod was positioned in a silica glass tube of internal diameter 3.6 mm, external diameter 5.6 mm and 30 mm long, by silicone rubber stoppers which

were held in place by tin foil at each end (Figure 1). This assembly was placed in a high pressure differential thermal analysis, d.t.a., cell with the thermocouple's metal sheath a press fit into the recess<sup>13</sup>. The d.t.a. cell comprised a high tensile steel tube with external heaters, filled with silicone oil which could be pressurized by a hand pump<sup>14</sup>. A large volume dielectric cell<sup>13</sup> was used as a ballast reservoir to prevent pressure change during the heating process.

Densification was carried out by heating the sample under the required pressure to a temperature some 20K above the glass transition *under pressure*, as determined from the step in the differential e.m.f. – temperature curve of the high pressure d.t.a. The maximum temperature was maintained for 30 min to allow the sample to equilibrate, it was then cooled, under pressure, at 1 K/min through  $T_g$  to room temperature when the pressure was released and the sample removed and stored below room temperature.

### Differential scanning calorimetry

A Perkin–Elmer DSC-2 with alumina as calibrant<sup>15</sup> was used; the heating rate was 20 K/min except where stated. Samples were scanned over a wide range of temperature so that all thermal events were preceded or followed by some 40–50K of 'normal'  $C_p$  behaviour. After a densified sample had been run it was cooled in the d.s.c. usually at 20 K/min, and rerun to provide a reference, one atmosphere glass; conversion of results for a –20 K/min glass to the more appropriate –1 K/min glass is discussed later.

Enthalpy differences between normal and densified glasses are small and are best measured by direct superposition of the relevant curves<sup>16</sup>. Clearly the liquid regions must superimpose but it was important to verify that this treatment was also valid for the two glasses. A 'backing off' technique was used. The bulk of the signal from the polymer was

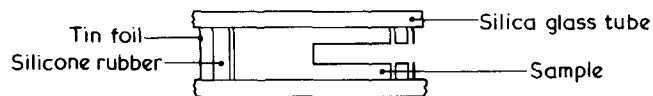


Figure 1 Detail of the sample holder used in densification

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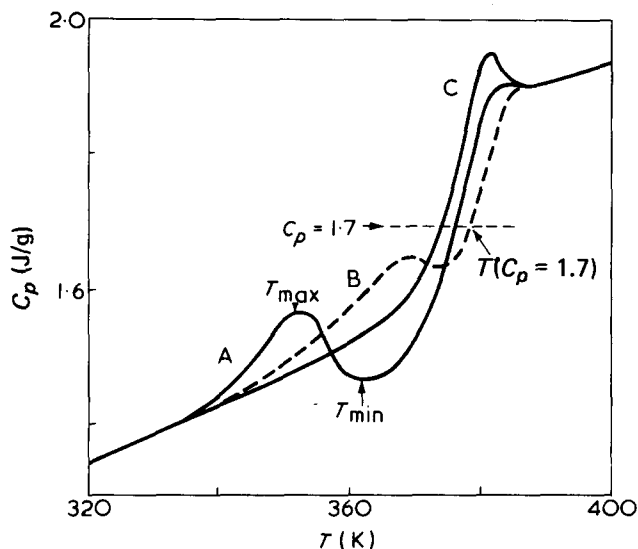


Figure 2 Specific heat curves (20K/min) for polystyrene glasses ( $M_n = 150\,000$ ) formed by cooling from the liquid at 1 K/min under the pressures shown. 'Reference' is formed at atmospheric pressure (0.1MN/m<sup>2</sup>) by cooling at 20 K/min. A, 310 MN/m<sup>2</sup>; B, 140 MN/m<sup>2</sup>; C, reference

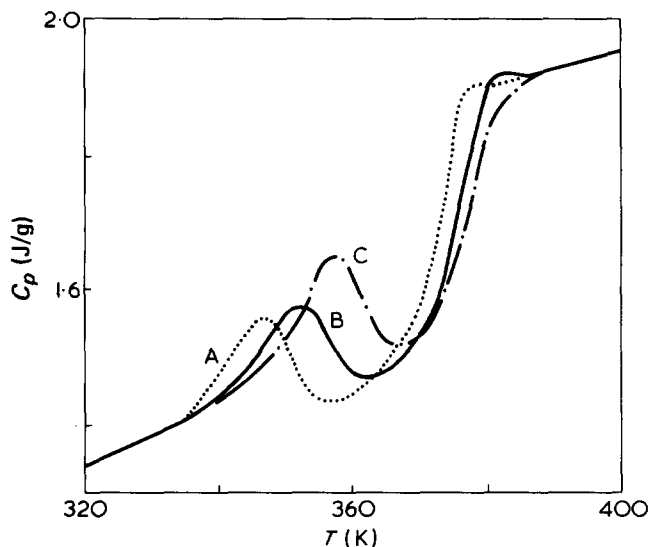


Figure 3 The effect of heating rate on the 310 MN/m<sup>2</sup> glass of Figure 2. A, 5 K/min; B, 20 K/min; C, 40 K/min

backed off by alumina in the normally empty 'reference' pan so that the instrument could be operated at maximum sensitivity. The densified glass was then run between, say 280–320K, taken through  $T_g$ , cooled at 20 K/min, and rerun over the same range. Subtraction of the curve for the –20 K/min glass from that of the densified glass showed that in all cases  $\Delta C_p < 0.1\%$  and it is therefore permissible to superimpose the glassy regions. The similarity of  $C_{pg}$  is not surprising when compared with the rather small (1%) difference between two very different structures, a glass and a crystal<sup>17</sup>.

Glass temperatures were calculated as described previously<sup>12</sup>.

## RESULTS

The main variables in the d.s.c. experiments were densification pressure and heating rate  $R$ , the latter because, although  $R = 20$  K/min was standard for most runs, some variation was

essential to allow a comparison of d.s.c. results with those of dilatometry ( $R = 0.5$  K/min). Densification (Figure 2) introduces an apparent endothermic peak which shifts to lower temperatures with increase in pressure, it is followed by a specific heat discontinuity typical of the glass transition of an unannealed glass. The latter is relatively unaffected by heating rate, Figure 3 (3.7K as  $R$  increases from 5 to 40 K/min, using  $T(C_p = 1.7)$ , Table 1, as an arbitrary measure to locate this transition) compared with the endothermic peak shift,  $T_{max} = 10.2$ K (Table 1) over the same range  $R$ . Glass transition temperatures  $T_g(H)$  calculated from the intersection of enthalpy curves for the glass and liquid<sup>12</sup> are shown in Tables 1 and 2, the 'thermodynamic' definition of  $T_g(H)$  gives a quantity that is independent of heating rate, Table 1, and all available data are incorporated into the average values of Table 2, the standard deviation is  $\pm 1.0$ K. Outside the transition region ( $<330, >390$ K) all curves superimpose.

Figures 4 and 5 show the specific volumes of polystyrene samples with the same history as those of Figure 2 except that the 'reference' glasses were cooled at 1 K/min. At low temperatures curves for the densified and reference glasses are approximately parallel but at temperatures well below  $T_g(V, \text{reference})$  there is a change of slope which would normally be associated with the glass transition. The volume slowly returns to that of the reference;  $T(V_d = V_r)$ , Table 2, is that temperature at which this first occurs. Glass temperatures  $T_g(V)$ , Table 2, were found by linear extrapolation of  $V-T$  curves from outside the transition region; a quadratic temperature fit has been found to be a better representation of the data for anionic polystyrenes<sup>18</sup> but curvature is only significant over wide ranges of temperature.

Entropy,  $S$ , as well as enthalpy, changes can be calculated from the  $C_p$  curves of Figure 2. In the present case 'point' values of  $C_p$  are available at intervals of a few tenths of a degree and it is convenient to calculate each entropy increment as  $C_p \Delta T / T_{av}$  where  $\Delta T \sim 0.5 = T_j - T_i$ ,  $T_{av} = (T_i + T_j)/2$ . Summation gives the apparent entropy change over any desired temperature range and it is normal to make the upper limit some convenient point in the liquid (400K in the following example). The 'apparent' nature of the enthalpy changes so calculated must be emphasized. Although

Table 1 The effect of heating rate on d.s.c. curves of a polystyrene glass formed at 310 MN/m<sup>2</sup>

Rate (K/min)	$T_{max}^*$ (K)	$T_{C_p = 1.7}^*$ (K)	$T_g(H)$ (K)
5	347.2	373.5	374.1
20	352.1	376.0	373.7
40	357.4	377.2	373.2

\* Defined in Figure 2

Table 2 Temperature characteristics (at 20 K/min) of densified polystyrene ( $M_n = 150\,000$ ) glasses

Treatment	Temperature (K)				
	$T_{max}$	$T(C_p = 1.7)$	$T_g(H)$	$T_g(V)$	$T(V_d = V_r)$
Reference glass	—	373.3	372.4	365.2	—
140 MN/m <sup>2</sup>	369.7	378.4	373.8	339.2	362.7
310 MN/m <sup>2</sup>	352.1	376.0	373.7	328.4	362.2

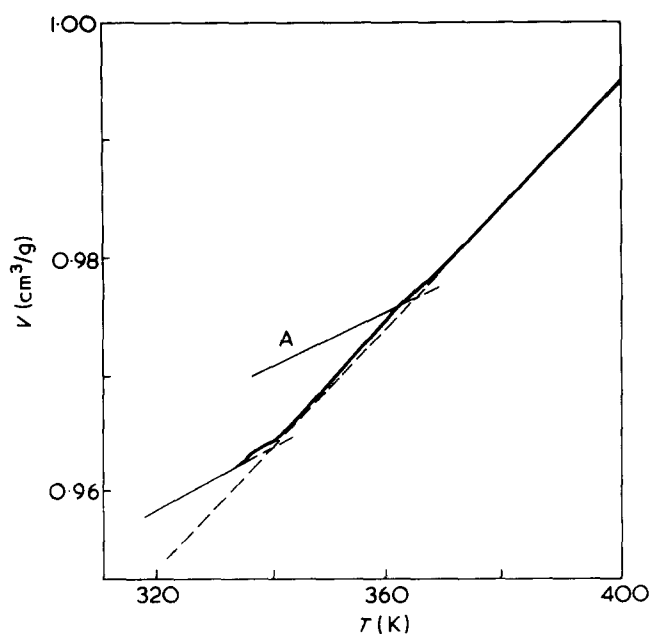


Figure 4 Specific volume-temperature curves for the 140 MN/m<sup>2</sup> glass of Figure 2. A, 'Reference' is formed at atmospheric pressure by cooling at 1 K/min

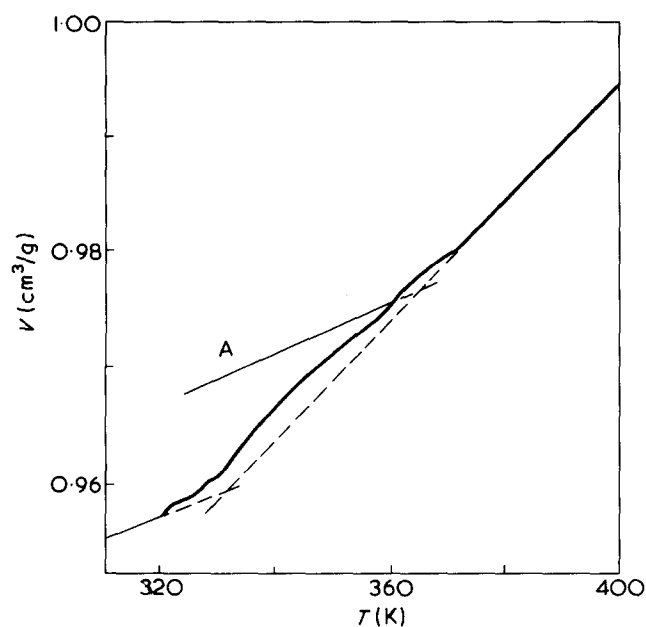


Figure 5 As Figure 4 but glass formed at 310 MN/m<sup>2</sup>. A, reference

the total enthalpy change is a true thermodynamic quantity its overall distribution is affected by the dynamic nature of a d.s.c. experiment. Two competing effects are involved: for equilibrium conditions a slow heating rate is needed but to prevent annealing changing the glass conformation, rapid passage through  $T_g$  is essential. In the present work attention is focused on variations between different glasses and in this respect irreversible entropy effects should at least tend to cancel. The differing effects of rate on  $T_{max}$  and  $T(C_p = 1.7)$  show that this can only be an approximation and the entropy and free energy,  $G$ , differences now to be considered should be taken only as qualitative illustrations. If  $Z$  is the reference temperature in the liquid, experimental quantities are  $H(T) - H(Z)$  and  $S_i(T) - S(Z)$  where the subscript 'i'

emphasizes irreversible contributions, and the free energy change is:

$$G_i(T) - G(Z) = H(T) - H(Z) - T[S_i(T) - S(Z)] - (T - Z)S(Z)$$

The liquid contribution vanishes when results for densified and reference materials are combined:

$$\Delta X(T) = X(\text{densified}, T) - X(\text{reference}, T)$$

where  $X = H, S_i$ , or  $G_i$ . Figure 6 shows these quantities for the materials of Figure 2. The curves of Figure 6 were obtained from individual  $C_p$  curves which did not exactly superimpose. Reproducibility is better than 1% but even this can lead to gross inaccuracy in  $\Delta H$  as this is a small difference ( $-1$  to  $+2$  J/g) between two large quantities  $H(300\text{K}) \rightarrow H(400\text{K}) \sim 150$  J/g. More reliable estimates of  $\Delta H$  are obtained by deliberately superimposing the non-transition (i.e. the glass and liquid limits) regions as justified in the experimental section. The data of Table 3 were obtained in this way.

Enthalpy data alone give ambiguous answers in that  $T_g(H)$ , Table 2, appears to decrease for the maximum densification pressure but it must be remembered that the error on all  $T_g(H)$  values is  $\pm 1^\circ\text{C}$ . The important result is that  $T_g(H)$ , as here defined is relatively unaffected by densification where  $T_g(V)$  shows large changes (this is shown schematically in Figure 7).

## DISCUSSION

A formal comparison of calorimetric and specific volume data requires the former to be presented as enthalpy curves,

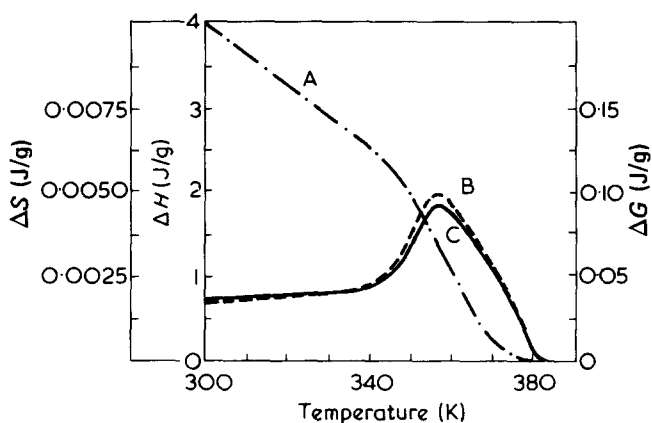


Figure 6 Changes between the thermodynamic properties  $X (= H, S$  or  $G)$  of densified and 'reference' polystyrene ( $M = 150\,000$ )  $\Delta X = X(310\text{ MN/m}^2, -1\text{ K/min}) - X(0.1\text{ MN/m}^2, -20\text{ K/min})$ . A,  $\Delta G$ ; B,  $\Delta S$ ; C,  $\Delta H$

Table 3 Enthalpy relative to normal glasses

Densification pressure $P$ (MN/m <sup>2</sup> )	$M_n$	$H(P, -1\text{ K/min}) - H(0.1, -1\text{ K/min})$ (J/g)
140	10 400	-0.70
	36 000	-0.98
	150 000	0.90
310	150 000	1.78
	2 000 000	2.18
345	19 800	2.04

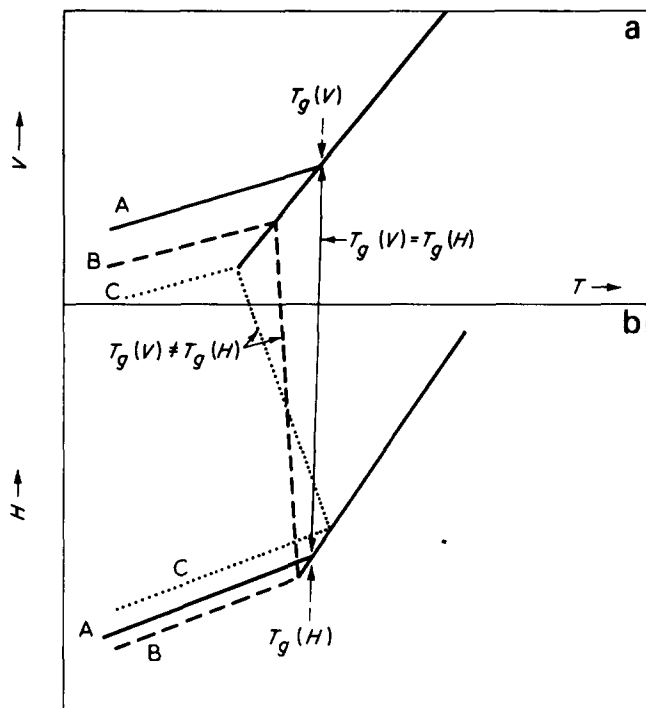


Figure 7 (a) Schematic specific volume – and (b) enthalpy – temperature curves showing the differing effects of pressure on  $T_g(H)$  (little affected) and  $T_g(V)$  (large changes). A, reference (1 atm); B, moderate and C, high densification pressures

rather than their derivative, the specific heat, the usual product of a d.s.c. measurement. The transformation from one to the other is a trivial operation with modern computational assistance but it has little value in the present circumstances because the slopes of the glassy and liquid regions are relatively close compared with  $\phi_g$  and  $\phi_l$ , where  $\phi = \partial V/\partial T$  and the detailed geometry of an enthalpy curve is best inferred from d.s.c. results. A direct comparison of the two sets of curves can only be made after a reduction of d.s.c. data to  $R = 0.5$  K/min. This can be accomplished using the observed linear relationship (Table 1) between  $T_{max}$  and  $\log |R|$  (and hence  $T_{min}$  since  $T_{max} - T_{min} \sim 10^\circ$ ). 'Peak' and 'trough' temperatures become 337 and 347K, respectively, for the broad molecular weight sample densified at 310 MN/m<sup>2</sup> and these are in good agreement with the points of maximum (336K) and minimum (345K) slope of Figure 5. Formally, therefore, enthalpy and specific volume measurements correlate well until  $T_g(H)$  and  $T_g(V)$  are compared. The comparison focuses attention on the contrasting behaviour of specific volume and enthalpy at room temperature. In themselves these, in the form  $\Delta X = X(\text{densified}) - X(\text{reference})$ , where  $X = H$  or  $V$ , are a good measure of  $\Delta T_g = T_g(\text{densified}) - T_g(\text{reference})$  since the curves are approximately parallel in the glassy state, being little affected by previous history (e.g. see Figures 4 and 5, also  $C_p(\text{densified}) \sim C_p(\text{reference})$  as already described). Clearly, if  $X = V$ ,  $\Delta X$  must always be negative, since compression can only give a decrease in volume, and  $T_g(V)$  will always be reduced. The situation when  $X = H$  is more complex. Table 3 shows the enthalpy differences between densified and reference glasses for a variety of molecular weights. Data for the  $-20$  K/min reference glasses of most experiments have been transformed to the more appropriate  $-1$  K/min glass by a correction term  $\Delta C_p \Delta T_g$  where  $\Delta C_p = C_{pl} - C_{pg}$  and  $\Delta T_g$

is the difference in glass temperature between the two glasses. The correction is about 0.9 J/g, an important contribution to the data of Table 3 and one which emphasises the need for careful characterization of thermal history. Weitz and Wunderlich<sup>5</sup> and Price<sup>9,10</sup> have studied enthalpy differences between densified and normal glasses, the former by d.s.c. and the latter using a Calvet calorimeter, and our data are in agreement with theirs. The present results tend to support the enthalpy–densification pressure curve<sup>5</sup> which suggests a slight minimum before  $\Delta H$  becomes a steadily increasing positive quantity with increase in pressure. A stronger statement cannot be made because the values given in Table 3 are thought to have errors of  $\pm 0.5$  J/g associated with them and thus obscure the finer details of the curve. Irrespective of this there can be no doubt that  $\Delta H$  is positive at high densification pressures, the very reverse of  $\Delta V$ , so that  $T_g(V)$  and  $T_g(H)$  appear to diverge with increase in densification pressure. For glasses prepared at atmospheric pressure there is agreement between  $T_g(H)$  (368.4K) and  $T_g(V)$  (365.7K); both these values refer to glasses formed at  $-1$  K/min and the reference  $T_g(H)$  value of Table 1, which refers to a  $-20$  K/min glass, has been reduced by 4.0K following subsidiary experiments on glasses formed under a variety of cooling conditions<sup>12</sup>. The general effect of densification pressure on  $T_g(H)$  and  $T_g(V)$  is shown schematically in Figure 7, in no way can the conflicting behaviour of the two be reconciled and the concepts involved in the use of  $T_g(H)$  or  $V$  must be re-examined.

The equilibrium conformation of a molten amorphous polymer is a function of temperature and pressure. By varying the cooling rate the molecules can be frozen-in at relatively high temperatures (quenching) or can relax to low energy states (slow cooling) giving a dependence of  $T_g$  on thermal history even at atmospheric pressure ( $\Delta T_g = 4.0$  K for the  $-20$  and  $-1$  K/min glasses discussed above). When a densified polymer is heated at atmospheric pressure the relevant liquid curve can never be attained and the 'one atmosphere' liquidus merely becomes a somewhat arbitrary, albeit experimentally convenient, reference line. Formally,  $T_g(H)$  or  $V$  can still be used to define temperatures that characterize a given history but agreement between the two should not be expected for densified glasses, the relatively large change from  $\phi_g$  to  $\phi_l$  with respect to that from  $C_{pg}$  to  $C_{pl}$  will give very different points of intersection ( $T_g$ ) for equivalent 'reference' lines. The source of the apparent endotherm of Figure 2 or 3 is now suggested: it is an attempt by the densified glass to undergo a glass transition but the molecular conformation is such that the requisite liquid is unstable and the glass falls back into a new higher volume (Figures 4 and 5) enthalpy and entropy (Figure 6) glass which progressively relaxes until a stable liquid is available as the transition product, this occurs near the normal glass transition.

Densified glasses probably lie in high energy conformations as suggested by Gee<sup>19</sup>, these are the 'flexed bonds' of the Gibbs and DiMarzio theory<sup>20</sup>. From this point of view an equivalent explanation is to consider the endotherm as an uptake of energy (Figure 2) which allows an increase in free volume, when this has occurred there are enough Gibbs–DiMarzio 'holes' for the chains to relax from their high energy states and  $\Delta H$  falls (Figure 6). Enthalpy (via  $C_p$ ) and specific volume curves mutually support this hypothesis. Corresponding temperatures (e.g.  $T_{max}$ ) on the two curves agree well (after allowance for the different heating rates) and the only differences are in either indirect quantities [such as  $T_g(H)$  or  $V$ ], and it has already been seen that these

will not agree] or the sign of  $\Delta X$  after densification at any pressures.  $\Delta V$  can only be negative and this must initially also be the sign of  $\Delta H$  as free volume is minimized with consequent reduction in 'hole' enthalpy, the sign changes when molecular repulsion becomes significant. Although the low temperature of the attempted glass transition is at first surprising, in view of the known increase of  $T_g$  with pressure<sup>4</sup>, it must be recalled that all experiments were carried out at atmospheric pressure.

The schematic diagram, *Figure 7*, compares the usual definition of  $T_g(V)$  for a glass formed at high densification (curve *C*) with  $T_g(H)$ . In both cases data are extrapolated from outside the transition region to give a discontinuity defining the respective glass transitions. As we have already discussed, *Table 2*,  $T_g(V)$  under these conditions may easily be 40K lower than  $T_g(H)$ . The question arises therefore as to the physical nature of the material between these two alternative definitions of  $T_g$ . Dynamic modulus experiments will shortly be reported<sup>2f</sup> which show that below the upper transition point  $T_g(H)$  the modulus is typical of a glassy rather than a rubbery state. This supports the concept that the 'phase' intermediate between the two thermal events of *Figures 2* and *3* is a modified glass.

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#### REFERENCES

- 1 Shiskin, N. I. *Sov. Phys. Solid State* 1960, **2**, 322
- 2 Dale, W. C. and Rogers, C. E. *J. Appl. Polym. Sci.* 1972, **16**, 21
- 3 Kimmel, R. M. and Uhlmann, D. R. *J. Appl. Phys.* 1970, **41**, 2917
- 4 McKinney, J. E. and Goldstein, M. *J. Res. Nat. Bur. Stand. (A)* 1974, **78**, 331
- 5 Weitz, A. and Wunderlich, B. *J. Polym. Sci. (Polym. Phys. Edn)* 1974, **12**, 2473
- 6 Wetton, R. E. and Money Penny, H. G. *Br. Polym. J.* 1975, **7**, 51
- 7 Yourtee, J. B. and Cooper, S. L. *J. Appl. Polym. Sci.* 1974, **18**, 897
- 8 Kimmel, R. M. and Uhlmann, D. R. *J. Appl. Phys.* 1971, **42**, 4917
- 9 Price, C. *Polymer* 1975, **16**, 585
- 10 Price, C., Williams, R. C. and Ayerst, R. C. 'Amorphous Materials' (Eds R. N. Douglas and B. Ellis) Wiley-Interscience, London, 1972, Ch. 12 p 117
- 11 Kovacs, A. J. *Rheol. Acta* 1966, **5**, 262
- 12 Richardson, M. J. and Savill, N. G. *Polymer* 1975, **16**, 753
- 13 Warner, F. P. *PhD Thesis* Loughborough University of Technology, 1975
- 14 Pressure Products Industries, High Pressure handpump OH-101-150
- 15 Richardson, M. J. *J. Polym. Sci. (C)* 1972, **38**, 251
- 16 Marshall, A. S. and Petrie, S. E. B. *J. Appl. Phys.* 1975, **46**, 4223
- 17 Chang, S. S. and Bestul, A. B. *J. Chem. Phys.* 1972, **56**, 503
- 18 Richardson, M. J. and Savill, N. G. *Polymer* 1977, **18**, 3
- 19 Gee, G. *Contemp. Phys.* 1970, **11**, 313
- 20 Di Marzio, E. A., Gibbs, J. H., Fleming, P. D. and Sanchez, I. C. *Macromolecules* 1976, **9**, 763
- 21 Wetton, R. E. and Brown, I. G. to be published