Glass Transition Measurements on Polystyrene by Differential Scanning Calorimetry

A. LAMBERT*

We have developed a method of measuring the glass transition temperature of a polystyrene sample using a Perkin–Elmer differential scanning calorimeter DSC-1. As the temperature of the sample rises through the glass transition we find a clear endotherm of about 0·92 cal/g polystyrene. This value agrees with other experimental evidence and is supported by theoretical consideration. The DSC–1 glass transition temperature is closely related to softening point measurement by the B.S.2782 cantilever test.

THE glass transition temperature of a sample of polystyrene is one of the important parameters governing the applications for which the grade can be used. *B.S. 2782* Part 1, Method 102C describes a simple cantilever softening point test which, since softening point is closely related to the glass transition, gives an adequate measure of T_g for most commercial grades. However, this test cannot be used for those experimental grades which are either not available in sufficient quantity or have so low or so high a molecular weight that they are difficult to mould. These limitations do not apply to a test method we have developed using the Perkin–Elmer differential scanning calorimeter (DSC-1).

Using equipment similar in principle to the DSC-1 in an oxygen-free atmosphere, Wunderlich and Bodily[1] showed that the thermal change associated with the glass transition is most marked when the polystyrene sample has been slowly cooled and then tested at a fast heating rate, rather than when it has been quenched and tested at a slow heating rate. We thus developed our own slow cooling technique and found the most convenient heating rate to be used on the DSC-1.

EXPERIMENTAL

Cooling and sample encapsulation technique

Using 'Carinex' HR as the sample we compared three methods of cooling and encapsulation. The last two involved simultaneous cooling and encapsulation of the polystyrene ready for insertion into the test position on the DSC-1.

Method 1—0·5 g of polystyrene was placed in a small glass vial and heated in an oven from room temperature to 160°C in about 90 minutes and then cooled at 5 deg. C/hour to 25°C. Several 10 mg samples were ground from the 0·5 g lump and each encapsulated in a DSC-1 aluminium sample pan and cover.

*Present address: 'Shell' Research Ltd, Egham Industrial Chemicals Laboratory, P.O. Box 11, Egham, Surrey.

Method 2—10 mg encapsulated samples, with covers, were heated to 160°C on the DSC-1 in still air at 64 deg. C/minute scan speed. The capsules were left in the DSC-1 sample holder assembly with its cover on and allowed to cool in about three minutes from 160°C to about 30°C by natural heat loss.

Method 3—Several samples of 5, 10, 20 and 25 mg of polystyrene were placed in open DSC-1 aluminium sample pans and heated and cooled as described in Method 1, but under a nitrogen blanket. Sample pan covers were crimped on to the pans when they were cold.

Heating rate and DSC-1 operating technique

In an atmosphere of still air or a nitrogen stream of 20 ml/min we used the four faster heating rates available on the DSC-1 (viz. scan speeds of 64, 32, 16 and 8 deg. C/min). The DSC-1 temperature indicator has to be calibrated against standards of known melting point. Because the thermal lag between the sample and the temperature sensor on the DSC-1 depends on scan speed we found that, when the DSC-1 is calibrated at a low scan speed, the indicated temperature is too high at faster scan speed. We calibrated the instrument at 8 deg. C/min using indium and lead standards. We also scanned these standards at 16, 32 and 64 deg. C/min to determine the corrections to apply to the indicated temperature at these scan speeds. As shown in *Table 1*, at each scan speed the ratio of the correct to the indicated temperature in °K was the same for both indium and lead. This ratio was taken to apply over all the range of temperatures of interest.

The DSC-1 can measure the magnitude of an energy change as well as the temperature at which it occurs. We determined the energy calibration

Table 1. Corrections for thermal lag at fast scan speeds

(a) Raw data

Sample atmosphere		Indicated melting point (°K) at various scan speeds*			
		8 deg. C/min	16 deg. C/min	32 deg. C/min	64 deg. C/min
Indium	N₂ stream	428	428·5	431	435·5
	Still air	428	429·5	432	438·5
Lead	N₂ stream	600	601	604·5	610
	Still air	600	602	605·5	613

*Sample holder covers on during all experiments.

(b) Factors by which temperature in °K indicated on the DSC-1 must be multiplied in order to obtain correct temperature, °K

Atmosphere	Scan speed, deg. C/min		
	16	32	64
N₂ stream	0·998	0·993	0·983
Still air	0·997	0·991	0·977

of the DSC-1 by comparing calculated latent heats of indium and lead at 16 deg. C/min with their known values. The energy calibration is independent of scan speed.

Throughout the work the DSC-1 reference holder contained an empty sample pan and cover.

RESULTS

Cooling method

The three cooling methods are compared in *Figures 1* and *2*. The thermograms shown are for 10 mg samples and the temperature scales are not corrected for thermal lag at high scan speeds. Thermograms 1* and 3 (*Figure 1*) show that Method 1 (using oven-and-air-cooled granular samples tested in still air) can give a thermogram with a well defined endothermic peak at the glass transition (117°C) but, if thermal contact between the grains is bad, then the thermogram is irregular and the glass transition endotherm is not clear. We designate the temperaure at the top of the peak as the glass transition temperature. Thermograms 2 and 4 obtained in still air show that cooling Method 2 (in the DSC-1 test position) eliminates the problem of bad thermal contact between grains but reduces the definition of the glass transition endotherm compared to Thermogram 1. Thermogram 8 (*Figure 2*), obtained in a stream of nitrogen, shows that cooling Method 3 (cooling in sample pans in nitrogen in oven) gives an extremely well defined glass transition endotherm. There is again no problem of thermal contact. Additionally the use of an oxygen-free atmosphere during cooling prevents the browning of the samples due to oxidative degradation noted in the first two cooling methods.

Clearly Method 3 is best. We consider it satisfactory for the accurate measurement of glass transitions in polystyrene in the DSC-1.

Effect of scan speed

It is well known that the glass transition is a time-dependent as well as temperature-dependent phenomenon, so it is to be expected that the glass transition temperature will change with scan speed. Therefore, in order to obtain comparative results from different equipment using different heating rates, it is necessary to obtain glass transition temperatures on the DSC-1 at several scan speeds and extrapolate either to zero speed or to a standard speed (see below).

The effect of scan speed on the DSC-1 thermogram is illusrated in *Figures 1* and *2*. Again, the temperature scales are not corrected for thermal lag at high scan speeds, but this is a minor change compared to the movement of the peak of the glass transition endotherm.

Thermograms 4, 5, 6 and 7 (*Figure 1*) obtained from cooling Method 2, show that as scan speed decreases the endothermic peak becomes less distinct and moves to a lower temperature. Thermograms 8, 9, 10 and 11 (*Figure 2*) obtained from cooling Method 3 show the same pattern, but here, at the lowest scan speed (8 deg.C/min), the transition peak is still well defined.

---

*The difference in the grades of polystyrene between thermograms 1 and 2 and the remainder is unimportant in the context of the points made here.

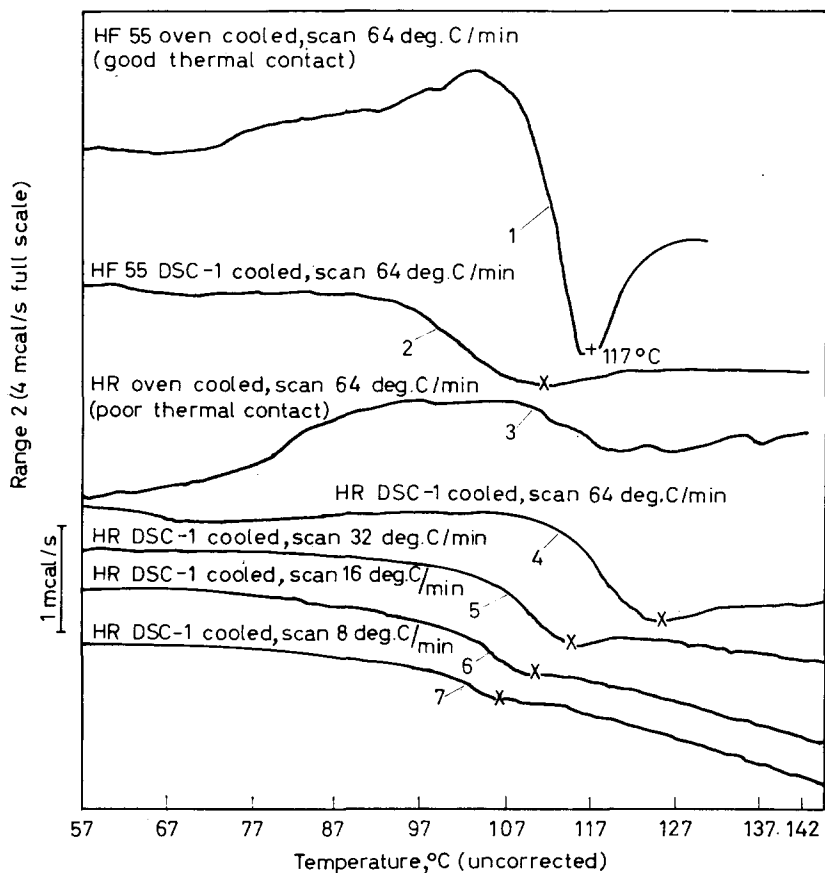*Figure 1*—DSC-1 thermograms. Effect of thermal history, sample form and scan rate on T_g. (Cooled in air either on DSC-1 or in oven.) 1 HF 55 oven cooled, scan 64 deg. C/min (Good thermal contact). 2 HF 55 DSC-1 cooled, scan 64 deg. C/min. 3 HR oven cooled, scan 64 deg. C/min (poor thermal contact). 4 HR DSC-1 cooled, scan 64 deg. C/min. 5 HR DSC-1 cooled, scan 32 deg. C/min. 6 HR DSC-1 cooled, scan 16 deg. C/min. 7 HR DSC-1 cooled, scan 8 deg. C/min

Effect of sample holder covers

The use of sample holder covers reduces the thermal lag between the sample and the temperature sensor and hence increases the accuracy of the indicated transition energy. An example of this is seen in *Table 2*. The glass transition temperatures are all higher when the sample holder covers are not used.

Effect of sample weight

Statistical analysis by the Kruskal–Wallis test of the results in *Table 2* at 16 deg. C/min scan speed shows that there is a 90 per cent probability that the DSC-1 shows larger samples undergo their glass transition at a
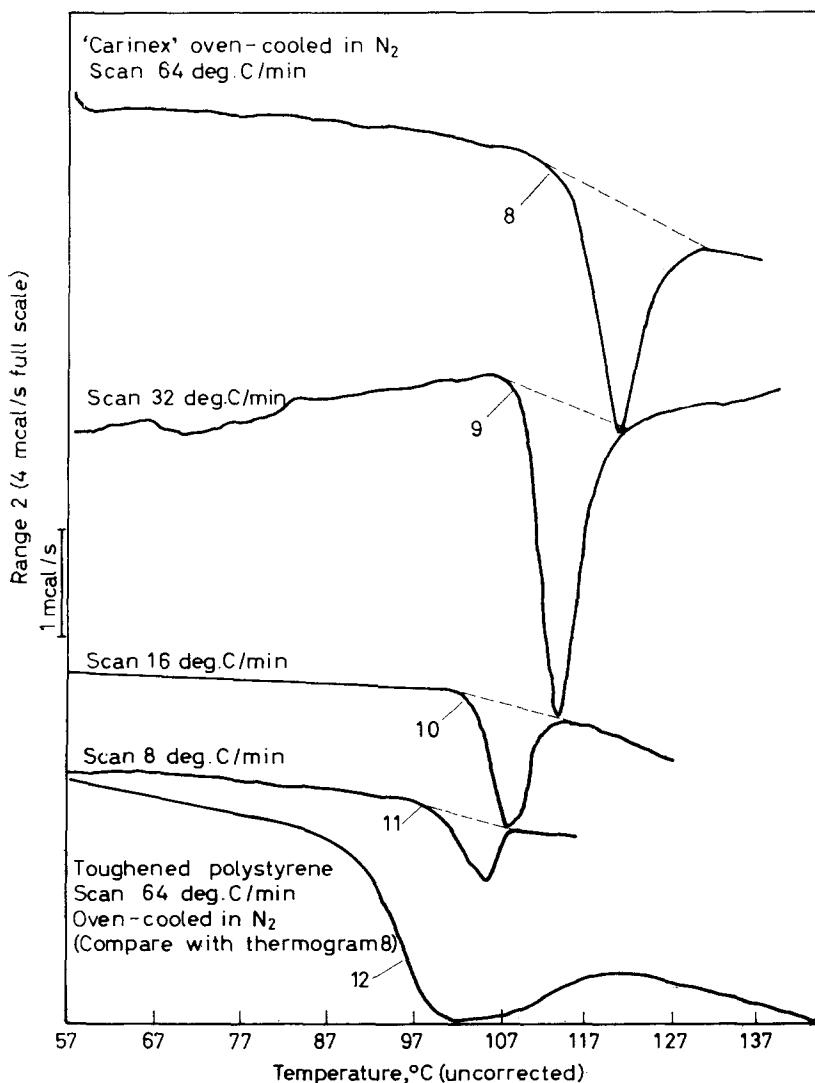
322

Figure 2—DSC-1 thermograms. Effect of scan rate on T_g of Carinex HR oven cooled in nitrogen, also a comparative thermogram of toughened polystyrene. 8 Scan 64 deg. C/min. 9 Scan 32 deg. C/min. 10 Scan 16 deg. C/min. 11 Scan 8 deg. C/min. 12 Toughened polystyrene, scan 64 deg. C/min. (Compare with thermogram 8)

higher temperature. At other scan speeds the probability is less but, overall, larger samples undergo their glass transition at significantly higher temperatures. This is to be expected because thermal lag should increase with sample size.

Glass transition temperature of 'Carinex' HR nibs

The results in *Table 2* (excepting those obtained using sample holder

covers) are corrected for scan speed from *Table 1* and are plotted in *Figure 3*. It is tempting to extrapolate data to zero scan speed but it is not clear if the concept of an isothermal glass transition is meaningful. The scan speed scale is thus chosen to be logarithmic and, to make the DSC-1 and the B.S. tests comparable, the DSC-1 results are extrapolated to the

Table 2. Glass transition temperature of 'Carinex' HR as a function of scan speed, sample weight and use of sample holder covers

Scan speed (deg. C/min)	T_g (°C)* for sample weight of:			
	5 mg	10 mg	20 mg	25 mg
8		106†		105·5†
	107	108	108·5	
	108	106·5	107	
16		109†		108†
	110·5	111	112	
	109·5	111·5	112	
32		114†		114†
	115·5	117·5	117	
	117		117·5	
64		122†		121†
	124	126	126	
	125·5	126·5	125	

*Annealing Method 3. Samples tested in nitrogen stream.
†Sample holder covers used. No suffix means sample holder covers not used.

1 deg. C/min heating rate used in the B.S. test. This intercept is still ambiguous unless we also, for each scan speed, first extrapolate our data to some consistent sample weight such as that of the indium and lead calibration standards (about 5 mg). These two extrapolations give

$$T_g = 104° \pm 1°C$$

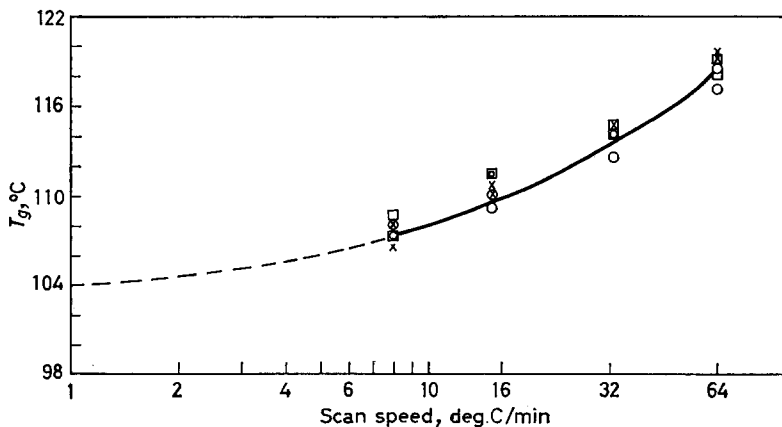*Figure 3—T_g* results for 'Carinex' HR, corrected for scan speed. ○ 5 mg samples. × 10 mg samples. □ 20 mg samples

324

The added accuracy obtained by the extrapolation to 5 mg sample weight is so doubtful that in practice the single extrapolation of data from 5 or 10 mg samples is satisfactory.

Latent heat of the glass transition

The endothermic peaks on thermograms 8–11 (*Figure 2*) are so well defined that we can measure the size of the energy change occurring during the transition. To do this we estimate the position of the baselines to be as shown by the dotted lines. Energy changes measured from thermograms 8–11 and others are listed in *Table 3*. We find an energy change equivalent to a 'latent heat of melting' of about 0·92 cal/g polystyrene.

Table 3. Latent heat of glass transition of 'Carinex' HR nibs annealed and tested in nitrogen

Scan speed (deg. C/min)	Latent heat (cal/g) for sample weight of:							
	5 mg		10 mg			20 mg		25 mg
64	–	0·70	0·84	–	1·38	–	–	0·92
32	0·72	0·66	0·72	1·06	1·22	–	–	1·24
16	1·12	0·78	0·62	0·84	1·37	1·08	0·94	0·86
8	0·66	1·12	0·88	0·78	1·76*	0·72	0·72	1·01

Mean=0·918±0·088 (with 95% confidence)

*Omitted from determination of mean.

DISCUSSION

Our results can be discussed in two parts. First from the experimental standpoint and then the theoretical.

Our mean latent heat of 0·92 cal/g is in agreement with the value of about 1 cal/g reported by Merrill and Gibbs[2]. The glass transition temperature we find for 'Carinex' HR nibs is three or four centigrade degrees higher than the B.S. cantilever softening point. This difference is not surprising since the point on the thermogram we designate as T_g, viz. the peak of the endotherm, is chosen for its ease of recognition and is not directly related to the softening point.

With toughened polystyrene the peak of the endotherm on the thermograms becomes less distinct (compare thermograms 12 and 9, *Figure 2*) and it becomes less easy to define a recognizable part of the thermogram as T_g.

Gee[3] shows that, at the glass transition, simple thermodynamics predict a latent heat

$$\Delta H = (dU/dV)_{T,P} \Delta V + P \Delta V \tag{1}$$

which leads to a value for polystyrene of about 0·8 cal/g in agreement with our experimental result. There is an unresolved difficulty, however, because if equation (1) holds then

$$V T_g \Delta\alpha/\Delta C_p = \Delta\beta/\Delta\alpha \tag{2}$$

which Gee shows to disagree with the experimental results. In these equations the symbols have the following meanings:

H enthalpy
U free energy
V specific volume
P pressure
T temperature
C_p specific heat at constant pressure
α temperature coefficient of volume expansion
β compressibility
ΔC_p etc. values in rubbery region minus values in glassy region

Wunderlich and Bodily[1] use the statistical mechanical theory of holes to explain why it is possible to obtain glass transition which is apparently a first order change complete with latent heat. They point out that, after slow cooling, a fast heating rate causes the equilibrium number of holes to be overshot since there is insufficient time for equilibrium to be set up. The sample returns to the equilibrium condition via a path which appears to be endothermic. Using Wunderlich and Bodily's values of the size and energy of a mean hole in polystyrene we calculate that our latent heat of 0·92 cal/g implies an overshoot equal to about 1·3% of the total polymer volume. If the free volume at the glass transition region is 10 per cent, as they suggest, or 13 per cent as is proposed by Bondi[4] and Haward et al.[5], then our overshoot of 13 per cent of the free volume seems reasonable.

'Shell' Research Limited,
  Carrington Plastics Laboratory,
    Urmston, Manchester.

REFERENCES

[1] WUNDERLICH, B. and BODILY, D. M. *J. Polym. Sci. C*, 1964, **6**, 137
[2] MERRILL, E. W. and GIBBS, J. A. *Chem. Engng News*, 1963, **41**, 41
[3] GEE, G. *Polymer, Lond.* 1966, **7**, 177
[4] BONDI, A. *J. Polym. Sci.* 1964, **A2**, 3159
[5] HAWARD, R. N., BREUER, H. and REHAGE, G. *J. Polym. Sci. B*, 1966, **4**, 375