Determination of the specific heat of polystyrene by d.s.c.

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(Received 4 August 1976; revised 27 September 1976)

The specific heat of various polystyrenes has been measured by d.s.c. using two methods—calibrating with heat of fusion of indium and using sapphire as an external standard. The effect of such variables as sample weight, heating rate and calorimeter sensitivity on the measurements are considered. In general, a limiting accuracy of 2% and temperature variations of 6K are imposed by these methods, and the detector response of the calorimeter.

INTRODUCTION

The measurement of specific heat, and related thermodynamic parameters, over a temperature range is important in relating the structure and properties of a polymer and in testing models for the glass transition, melting and crystallization, and polymerization and depolymerization kinetics. Accurate measurements are required to calculate entropy, enthalpy and free energy of polymers as a function of state.

We have recently required values of the specific heat of polystyrene as a function of temperature to calculate the linear expansion coefficient from the thermoelastic effect which in turn can be used to determine the Grüneisen constant (γ). This constant is an important parameter of a material[1] since it relates the pressure response of a solid to an energy deposition. From a thermodynamic standpoint it can be defined in terms of the internal energy derivative of the pressure at constant volume:

$$\gamma = (\partial p/\partial E)_v \cdot V$$

Variations, up to 10%, were observed in listed values for the specific heat of polystyrene[2] with a similar variation in their temperature dependence. These variations were considered too large and specific heats were measured directly on the samples under investigation, in order that the derived thermodynamic parameters had significance.

The present paper reports on the result of these measurements on specific heats and the possible source of these variations. It also considers the usefulness and limitations of d.s.c. in measuring rapid and accurate specific heats. Polystyrene alone was used in these investigations.

EXPERIMENTAL

Materials

Polystyrene samples from two sources were used: (a) monodispersed samples, Pressure Chemicals Co; their characteristics are listed in *Table 1*, and (b) the thermochemical standard-RAPRA PSCC PS2.

Calorimetry

Perkin–Elmer Differential Scanning Calorimeter, model DSC-2, was used with samples (5–40 mg) weighed to 0.1 mg, encapsulated in aluminium sample holders and operated in a stream of oxygen free nitrogen. Empty aluminium sample holders were used as references.

Temperature was calibrated from the melting points of zone refined benzoic acid, stearic acid, naphthalene and dibenzyl, and also ultra-pure metals, indium, tin and zinc. Observed m.p. values were dependent on sample weight and heating rate. Extrapolation to zero weight at constant rate or zero rate at constant weight were used to determine temperature corrections.

The heat of fusion of indium was taken to be 28.45 J/g in calibrating the calorimeter. Averaged over all settings of the calorimeter and some 30 determinations, a standard deviation of 2% was observed in this calibration.

Sapphire discs (0.131 g) were used as standards in the specific heat determinations. The specific heat–temperature data for sapphire determined by Ginnings and Furukawa[3] were used.

RESULTS AND DISCUSSION

General technique of d.s.c.

The measurement of specific heat by d.s.c. is an extension of the basic function of the calorimeter[4] since its primary function is to measure heat changes associated with a temperature rise of the sample at given rates. The recommended method of determining specific heat is to use an external standard (sapphire) and involves heating the standard and sample separately over the desired temperature range at fixed heating rates (5, 10 or 20 K/min). Deflec-

Table 1 Molecular weight characteristics

Sample no.	Osmotic $\times 10^3$	Viscosity $\times 10^3$	D*
1	19.8	19.6	1.06
2	10.9	10.5	1.06
3	5.20	4.7	1.10
4	2.07	2.03	1.10
5	0.93	1.22	1.10

*M_w/M_n, manufacturer's data

tions (D_p, D_s) from the base line, corrected for a blank empty aluminium sample pan, are proportional to the relative weights, (W_p, W_s) and specific heats (S_p, S_s) of the sample and standard, respectively (see *Figure 1*) provided the same calorimeter control settings are used, since:

$$S_p = (W_s/W_p)(D_p/D_s)S_s \qquad \text{J/K g} \qquad (1)$$

An alternative method involved calibrating the calorimeter in the temperature range of interest, i.e.

$$S_p = (D_p/W_p)\left(\frac{\text{Range}}{\text{Heating rate}}\right) 60\epsilon \qquad \text{J/K g} \qquad (2)$$

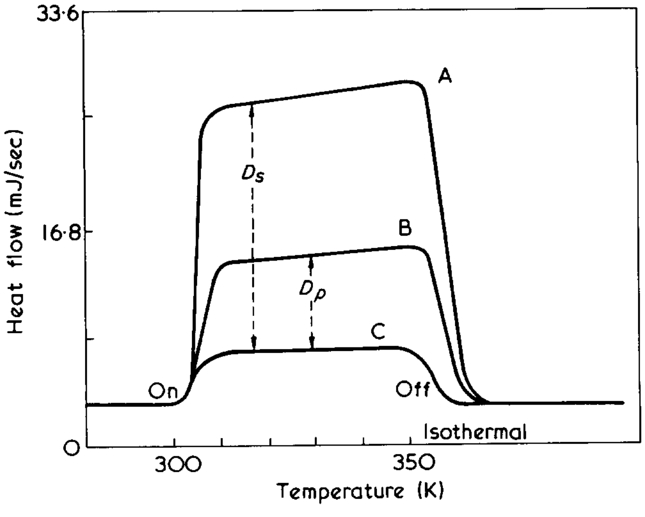

Figure 1 D.s.c. measurements on A, sapphire; B, polystyrene and C, base

where ϵ is the calibration correction per unit deflection. Using the heat of fusion of indium ϵ was determined as 4.174×10^{-3} mn^{-1}.

The determination of heat capacity involves measuring the deflection from a corrected base line and while there is a requirement to maximize this deflection there is also one of minimizing thermal lag between sample temperature and sensors. Accordingly the calorimeter sensitivity and heating rate were adjusted to give maximum deflection (above 100 mm). The recorder detector response had a quoted reproducibility of better than 1% but this could be substantially improved by a digital read out system. The specific heat values listed below have this limiting accuracy of ±1%. The effect of various instrumental settings and sample weight on the thermal lag and measured specific heats were considered.

Effect of heating rate and sample size

Specific heats were initially measured using equation (2), calibrating with indium, and the specific heat of sapphire was determined over the range 300–450K at various heating rates (2–20 K/min), since the sample had a mass of 0.131 g a large thermal lag was expected. The data determined is listed in *Table 2a*, along with the literature values[3] for comparison. A variation in measured specific heat of 1–2% was observed consistent with the accuracy in determining *D*. Temperature corrections for the thermal lag appear to be necessary since the measured specific heats are all 0.01–0.02 J/g K larger than the standard values. From the temperature dependence of C_p these differences corresponded to 5–10K temperature correction, similar trends were observed with the PS2 sample (see *Table 2b*) but since there was no standard values for comparison some measure of the thermal lag was gauged from the dependence

Table 2 Specific heats (J/g K) measured by equation (2)

(a) Sapphire

Rate of heating (K/min)	Temperature (K)							
	310	330	350	370	390	410	430	450
5	0.801	0.851	0.890	0.921	0.956	0.967	0.996	1.01
10	0.809	0.851	0.899	0.926	0.954	0.967	0.992	1.00
20	0.824	0.853	0.882	0.923	0.952	0.961	0.994	1.01
Ref 3	0.7996	0.8375	0.8715	0.9029	0.9306	0.9553	0.9773	0.9973

(b) Polystyrene PS2 (38.7 mg)

Rate of heating (K/min)	Temperature (K)					
	400	410	420	430	440	450
5	1.891	1.920	1.938	1.980	2.003	2.046
10	1.887	1.917	1.943	1.973	2.018	2.048
20	1.889	1.916	1.942	1.969	2.000	2.010
40	1.900	1.930	1.953	1.967	2.046	2.092

(c) Polystyrene PS2 heating rate 10 K/min

Weight (mg)	Temperature (K)					
	400	410	420	430	440	450
5.1	1.845	1.860	1.946	1.956	2.028	2.013
17.7	1.904	1.942	1.977	2.009	2.021	2.058
22.2	1.901	1.936	1.962	2.008	2.044	2.066
28.0	1.935	1.956	2.000	2.048	2.064	2.083
38.7	1.889	1.916	2.010	2.038	2.083	2.100

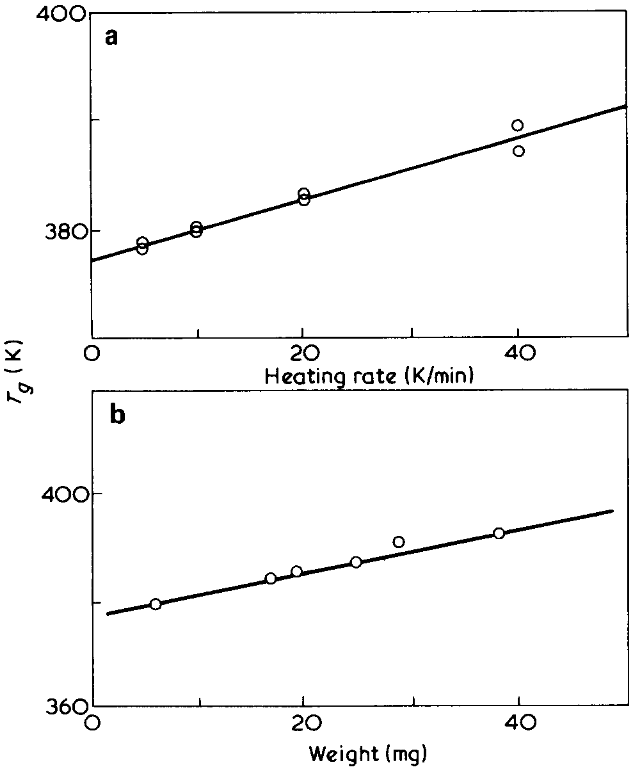

Figure 2 Glass transition temperature of PS2 effect of: (a) heating rate (25.0 mg); (b) sample weight (10 K/min)

of the glass transition temperature (T_g) on the rate of heating (see *Figure 2a*). For this purpose, the samples were initially heated to 450K and subsequently cooled at 10 K/min through the transition region in order to produce a standard glass. The measured value of T_g increased linearly with heating rate and indicated that substantial temperature corrections were required.

Specific heats and glass transition temperatures were also determined with different weights of PS2 in the range 5.0–40.0 mg (see *Table 2c*). This range was limited by the calorimeter detector response, limiting accuracy in weighing ±0.05 mg and the volume of the encapsulating pans. Determinations on 5.0 mg sample were less accurate than the other samples. No trend in the measured specific heats with sample size was observed within the accuracy of the determinations. T_g values, however, measured on samples with the same thermal history, indicated that a thermal lag was present and increased with sample size (see *Figure 2b*).

In further analyses using equation (2) standard conditions–a heating rate of 10 K/min and sample size of 25 mg–were used, and a temperature correction of 6K was applied for the thermal lag.

Comparison of equations (1) and (2)

Thermal corrections were used in the determination of specific heats using equation (2), since clearly some estimate of sample temperature can be obtained from the glass transition. However in the analyses using equation (1) a sapphire disc was used as an external standard for comparison with the PS sample. Both the standard and the sample will have associated thermal lags which are self compensating. Variations in calorimeter sensitivity, and heating rates are compensated for by comparison with the standard in this method. To some extent this is shown by the measured specific heats (see *Table 3a*) in that there is less variation between the measured values than observed previously (see *Table 2*) in analysing with equation (2) or alternatively when method (1) is used with the calorimeter setting varied to maximize the deflections (see *Table 3b*).

Measurements of specific heats by means of equation (1) would appear to have clear advantages over the alternative method (2), both methods do not appear to give the same measure of the specific heat, the first being substantially lower than the second. It was also not possible to assess the effect of thermal lag differences between the sapphire and the polystyrene samples. However, variations with heating rate suggest that there is an effect.

The lack of correlation between the two separate methods may be explained assuming that the sapphire external standard over-compensates for the thermal lag and a temperature correction is required which is larger than when equation (2) is used. Experimental variations within repeated determinations (0.02 J/g K) were less than those between determinations with different heating rates (0.04 J/g K).

Since it was not possible to measure the temperature correction equation (1) was not used in further studies despite the clear advantages of improved reproducibility.

Effect of sample history

In assessing accuracy, measurements were made on PS2 above the glass transition since time effects are marked in specific heat measurements on glasses[5]. An important factor in forming a glass is the heating rate through the glass transition temperature range and the duration time of the material in this range[5]. To assess the effect of this, samples of PS2 were cooled at various rates from 0.32 to 160 K/min from 450K and subsequently heated at the standard rate (10 K/min). At slow rates and the subsequent faster heating rates the volume and enthalpy of the glass tended to the lowest 'equilibrium' value but on subsequent heating this frozen-in structure is released above T_g. This accounts for the maximum observed in specific heats–temperature plots (see *Figure 3*) which were rate dependent. Rapid quenching through the transition resulted in higher specific heat values below T_g and the overall size of the effect can be gauged from *Figure 3*. Differences in specific heats between slow and fast cooling rates of up to 5% were observed but it is likely that even slower rates of heating or prolonged isothermal annealing at temperatures close to but below T_g under the correct conditions would produce greater differences. These annealing effects alone would account for the observed variations in the literature values of specific heats, and clearly reflect differences of sample preparation.

Table 3 Specific heats measured by equation (1)

Rate of Heating	Temperature (K)					
(K/min)	400	410	420	430	440	450
(a) Calorimeter settings fixed. 25.0 mg PS2						
5	1.826	1.885	1.891	1.901	1.970	2.010
10	1.827	1.893	1.926	1.946	1.974	2.030
20	1.842	1.870	1.910	1.972	2.003	2.048
(b) Calorimeter settings varied (X2). 25.0 mg PS2						
5	1.800	1.825	1.850	1.873	1.918	1.940
10	1.778	1.812	1.825	1.889	1.894	1.939
20	1.824	1.862	1.879	1.908	1.942	1.962

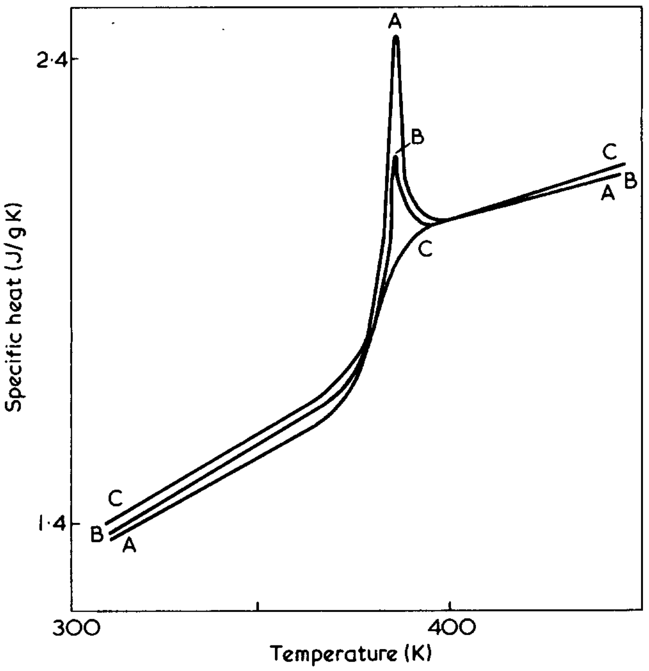

Figure 3 Specific heat dependence on glass structure. A, 0.32 K/min; B, 2.5 K/min; C, quenched

Table 4 Specific heats (J/g K): molecular weight dependence

Temperature (K)	Molecular weight × 10^{-3}				
	19.8	10.5	4.80	2.03	0.93
					above T_g
310	1.287	1.274	1.279	1.280	1.640
320	1.332	1.311	1.301	1.300	1.678
330	1.384	1.344	1.350	1.328	1.735
340	1.415	1.395	1.584*	1.987*	1.756
350	1.466	1.436	1.744*	1.802*	1.778
360	1.545	1.528	1.820	1.802	1.830
370	2.059*	1.728*	1.868	1.839	1.873
380	1.592*	2.020*	1.905	1.876	1.905
390	1.598*	1.970	1.965	1.908	1.947
400	2.004	2.031	2.007	1.963	1.989
410	2.041	2.041	2.026	1.987	2.021
420	2.051	2.078	2.081	2.037	2.074
430	2.084	2.084	2.098	2.066	2.096
440	2.099	2.138	2.122	2.123	2.137
450	2.157	2.182	2.146	2.160	2.169

* T_g region

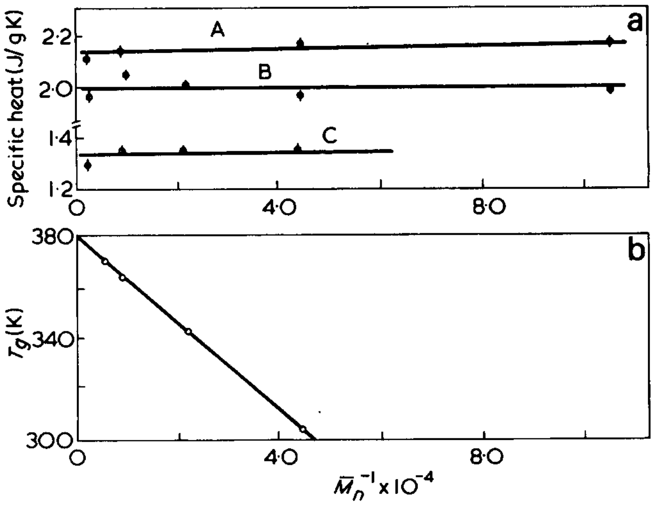

Figure 4 Molecular weight dependence of (a) specific heat: A, 450K; B, 400K; C, 330K; (b) glass transition temperature

Molecular weight dependence

Specific heat–temperature data of the monodisperse polystyrene samples were measured in the range 300–450K (see *Table 4*). There was no dependence of the measured specific heats on end group concentration (see *Figure 4a*). This was unexpected since the molar heat capacity of a molecule *n* monomer units long (C_p) is made up of two terms for the monomer units ($C_{p,m}$) and the two end groups ($C_{p,e}$), i.e.

$$C_p = nC_{p,m} + 2C_{p,e} \tag{3}$$

and so

$$S = S_m + 2C_{p,e}/M_n$$

S was invariant with $(1/\bar{M}_n)$ which meant that $C_{p,e}$ must be small compared with S_m. $C_{p,e}$ reflects the nature of the terminal unit and for the anionically polymerized material under discussion they would be H atoms. A larger effect would be expected with other PS samples.

The glass transition temperature, unlike the measured specific heats, exhibited a marked dependence on the number-average molecular weight (see *Figure 4b*) as predicted by the Flory–Fox[6] relationship:

$$T_g = T_g^0 - K/\bar{M}_n \tag{4}$$

but except for the region of this transition no large variation in specific heat was observed between the various samples as shown in *Table 4*.

CONCLUSIONS

D.s.c. measured specific heats are limited in accuracy by the recorder detector and could be substantially improved with a digital detector. In the present studies the accuracy of the determination is ±2%. Temperature corrections should be made for thermal lag due to sample weight and high rates of heating. Specific heats should be measured by direct comparison with a standard to reduce the effects of instrumental variations but it is then not possible to estimate temperature corrections. Variations in specific heats due to molecular weight depend on the nature of the end groups and with anionically prepared polymers were found to be negligible. Variations in the measured specific heats below the T_g due to structural variations in the glass are marked and a standard method of forming the glass is required. For the last reason it is recommended that the specific heats be measured directly on the polymer samples under investigation in deriving thermodynamic parameters rather than resorting to literature values.

ACKNOWLEDGEMENTS

The authors wish to thank Professor R. N. Haward for his encouragement and helpful advice, and the Science Research Council for financial support and provision of a maintenance grant (to I. W. G.).

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