Determination of specific heat of polystyrene by d.s.c.: 2

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(Received 19 April 1978; revised 8 May 1978)

INTRODUCTION

Specific heats of polymers have been conveniently measured by differential scanning calorimetry, (d.s.c.), and while there may be systematic errors inherent in the technique there are also sources of variation which determine the random error of the determinations.

In a recent publication[1] the limitations of d.s.c. in measuring specific heats of polystyrene were discussed. In general, it was concluded that the technique could not be used to the limiting response of the sensors because of the restrictions imposed by the data acquisition method, i.e. a 1–10 mV recorder and this could be substantially improved by digital display and computer analysis of the data. With the recorder, up to 2% variations were observed in the measured specific heats which masked trends due to sample size, heating rate and sample molecular weight although it was considered that these trends must be present.

A programmable calculator data acquisition system[2] for thermal analysis has been developed for d.s.c., and the characteristics which are quoted are at least 10 times better than those of the 10 mV recorder.

EXPERIMENTAL

The thermoanalytical polystyrene sample, PSCC PS2 (RAPRA) was used in these determinations in a restricted temperature range 400–450K. This range was set above the glass transition temperature to eliminate non-equilibrium glass effects and below the onset of thermal degradation.

A Perkin–Elmer differential scanning calorimeter, DSC-2, with Scanning Auto-Zero attachment with the PS samples 5–30 mg weighed to 0.001 mg, encapsulated in aluminium sample holders and operating in a stream of dried, oxygen-free, nitrogen. Empty sample holders were used as reference.

The temperature was calibrated from the melting points of pure metals, indium, zinc, tin and lead, by extrapolation of the observed melting points to zero weight at constant heating rates. The heat of fusion of indium was taken to be 28.45 J/g in calibrating the sensitivity of the calorimeter at various range settings.

Heat flow–temperature data were collected and processed by the Perkin–Elmer Programmable Calculator System, consisting of an interface module which converted the data into digital form for storing in the registers of a Tektronix model 31 Programmable Calculator. Up to four pairs of data points were collected per sec, and stored in sequence for analysis. The specific heat measurements were carried out automatically, instructions for the sequence of the measurements and the analysis of the data being read by the calculator from a programme stored on casette tape. Each determination was repeated five times. The interface could handle signals up to 120 mV with a resolution of 1 mV.

RESULTS AND DISCUSSION

The specific heat programme required prior calibration of the calorimeter over the range settings used in the experiment. Variations of up to 2% were observed in the measured sensitivity of the calorimeter at different range settings; accordingly values determined for each range setting were stored in the programme. Specific heat determinations involved measuring heat flow rates when heating the sample at various heating rates, correction being made for sample and reference differences by determining the specific heat of the empty aluminium holder. The reproducibility between runs could be gauged from repeated determinations on the aluminium sample holders. Averaged over ten determinations this was found to be ±0.002 J/g, and to be independent of range setting and heating rate.

Five determinations were made on each weight of PS 2 and at each heating rate. These are averaged in *Table 1*. The maximum variations between determinations are also listed. A linear plot of specific heat against temperature over the small temperature range of the measurements was observed, and a least square fit to the combined data from the five determinations. The variance of the data about the least square line was in the range $4–20 \times 10^{-6}$. Standard errors of the specific heats were 0.002–0.004 J/g.

The least squares estimated specific heats increased linearly with sample size at constant heating rate, and also with rate of heating at constant weight, see *Figure 1*. Values obtained by extra-

Table 1 Specific heat of PS 2

(a) Effect of heating rate on specific heat (J/g K); sample weight = 20.00 mg

	Temperature (K)					
K/min	400	410	420	430	440	450
0	2.075	2.125	2.175	2.227	2.285	2.345 ± 0.004
10	1.9625	2.001	2.039	2.078	2.117	2.155 ± 0.004
20	1.8327	1.876	1.919	1.963	2.007	2.050 ± 0.004
40	1.603	1.623	1.644	1.665	1.686	1.706 ± 0.004

(b) Effect of sample size; heating rate = 10.0 K/min

	Temperature (K)					
Weight (mg)	400	410	420	430	440	450
0.00	2.080	2.120	2.185	2.235	2.290	2.330 ± 0.004
8.80	2.025	2.055	2.104	2.163	2.210	2.248 ± 0.004
10.20	2.024	2.056	2.098	2.139	2.181	2.223 ± 0.004
15.76	1.982	2.012	2.053	2.094	2.135	2.166 ± 0.004
20.52	1.963	2.001	2.040	2.078	2.117	2.155 ± 0.004
22.75	1.946	1.979	2.013	2.047	2.082	2.114 ± 0.004

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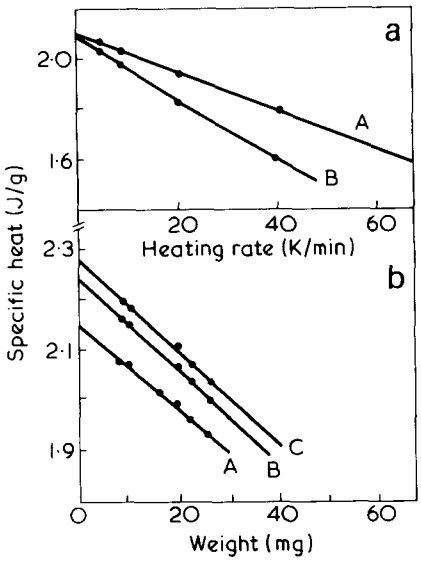

Figure 1 Dependence of the specific heat of PS 2 (a) on sample size A, 12 mg; B, 20 mg at 400K and (b) rate of heating. A, 430 K; B, 440 K ; C, 450 K

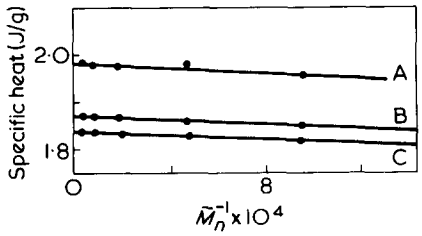

Figure 2 Molecular weight dependence of the specific heat of polystyrene. A, 420 K; B, 410 K; C, 400 K

polating to zero weight and zero rate were similar, and the two trends were consistent with thermal lags which increased with sample size and rate of heating. It was also consistent with the thermal lag correction applied previously[1] of 10K for a sample of 25 mg and a heating rate of 10 K/min.

The extrapolated specific heats, to zero weight and to zero rate, listed in *Table 1*, have been corrected for thermal lag. Both agree within the reproducibility of the determinations and so must represent the optimum values which can be measured by d.s.c. for this thermoanalytical standard. It would be meaningful to compare these values with those obtained by precision calorimetry in order to see if there are any systematic errors in d.s.c. measurement of specific heats.

Variations will be observed in the specific heats of different polystyrene samples. Accordingly monodisperse polystyrene samples (see ref 1, *Table 1*) were examined in the range 300–450K, in exactly the same manner as above. A small dependence of the specific heat on end-group concentration was observed, see *Figure 2*, consistent with equation (1) used previously[1]:

$$S = S_m + C_{p,e}/\bar{M}_n \qquad (1)$$

in which S and S_m are the specific heats observed and for the monomer repeat unit, and $C_{p,e}$ the average heat capacity for the end-groups. $C_{p,e}$ was found to be 20 ± 10 J/mol. $C_{p,e}$ must reflect the nature of the terminal units of the chain and so the mode of initiation, and will vary with polystyrene prepared by other methods.

CONCLUSIONS

Temperature corrections are required in measuring accurate specific heats of polymers by d.s.c., but conventionally these effects are masked by the limitations in accuracy of the determinations (±2%) imposed by the recorder used to detect the heat flow. A substantial improvement can be achieved if this is replaced by digital detection.

ACKNOWLEDGEMENT

The author wishes to thank Perkin–Elmer Ltd, Beaconsfield for the loan of equipment which made the measurements possible.

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Raman spectroscopic study of poly(vinyl chloride) particles

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(Received 19 April 1978)

INTRODUCTION

It has been shown[1] that when the growing chain of poly(vinyl chloride) attains a length of about 20 monomer units, it begins to precipitate from the liquid monomer. The chains agglomerate into so-called 'basic particles' which eventually reach about 200 Å in diameter.

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At this stage the basic particles form into clusters of diameter between 1000 and 2000 Å, called 'primary particles'. The polymer now begins to grow in a rather different way. No new primary particles appear, but the existing primaries slowly increase in size, not by further clustering, but by surface growth of successive polymer layers, rather like onion skins, until eventually polymerization ceases by monomer starvation. The change in the mode of growth of the polymer particles after the formation of primaries suggests that there may be an accompanying change in either the configuration or conformation of the polymer chain, or both, at this stage.

It is well known that both the configuration and conformation of a synthetic polymer chain may often be revealed by studying the vibrational spectrum. In vibrational studies of PVC, interest has centred particularly on the υ C–Cl (stretching) frequencies (see ref 2 and publications cited therein). By comparing the spectra of samples of different but known tacticity (i.e. of different molecular configuration) it has been possible to relate the appearance of υ C–Cl vibrations at particular frequencies to the presence of isotactic or syndiotactic sequences and, for the

0032–3861/78/101225–05$02.00