Thermochimica Acta, 179 (1991) 117–124
Elsevier Science Publishers B.V., Amsterdam

HEAT CAPACITY MEASUREMENT BY HEAT-FLUX-TYPE DSC ON COOLING AND HEATING CYCLES AT LOW SCAN RATES

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(Received 13 July 1990)

ABSTRACT

Heat capacity values (C_p) of sapphire and polystyrene were measured by heat-flux-type differential scanning calorimetry of both cooling and heating processes at scan rates ranging from 0.5 to 2.0 K $\min^{-1}$. The effects of heating rate and sample weight on the precision and reproducibility of the obtained C_p values of sapphire are discussed. A good standard deviation of the observed C_p values from the literature values was obtained for sample weights ranging from 10 to 20 mg and scan rates from 1.0 to 2.0 K $\min^{-1}$. The C_p values of polystyrene measured at 1.5 and 10 K $\min^{-1}$ on cooling and heating showed good agreement at the glassy state and super-cooled liquid state.

INTRODUCTION

In general, heat capacity measurements are carried out using a calorimeter under adiabatic conditions. Because it is difficult to maintain adiabatic conditions above room temperature, the experimental values may be in serious error at higher temperatures. Differential scanning calorimetry (DSC) has been shown to give satisfactory values of C_p [1–3]. Recently, C_p data measured by DSC were collected especially for polymeric materials [4–6]. The results of a round-robin test on the C_p measurements by DSC have also been reported for polystyrene [7].

Usually, C_p values by DSC are determined during heating. Although DSC cooling curves gave us important information on the super-cooled

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state, C_p values measured by DSC on cooling have rarely been reported. We have reported the effect of measuring conditions on the reliability of C_p using heat flux DSC during both heating and cooling at a scan rate ranging from 5 to 20 K min^{-1} [8]. The experimental conditions of 30 mg sample weight and 10 K min^{-1} scan rate gave the most precise values for C_p, for both heating and cooling processes. The experimental C_p of sapphire observed on cooling and heating at 10 K min^{-1} agreed with the literature values to within 0.5% of the relative standard deviation at temperatures ranging from 253 to 673 K [8].

As DSC is a dynamic procedure, the scan rate influences the accuracy and reproducibility of the values obtained. Most researchers use a scan rate of 10 or 20 K min^{-1} to measure C_p by DSC. In this study, C_p was measured on cooling and heating cycles at various scan rates ranging from 0.5 to 2.0 K min^{-1} using the highly sensitive heat-flux-type DSC; the precision and reproducibility of the obtained C_p values are discussed.

EXPERIMENTAL

Samples

The polystyrene (high impact type) sheet used for this study was the same as reported previously [7,9]. The sapphire used as a standard was a single crystal synthetic sapphire supplied by Seiko Instruments Inc. [8]. Sample weight was about 10, 20 and 30 mg, ± 1 μg.

Apparatus

Two heat-flux-type DSC instruments, a Seiko DSC 100 and DSC 200 connected to a Seiko SSC 5000 thermal analysis system, were used for this experiment. The automatic cooling accessory was equipped with DSC. The scan rates were 0.5, 1, 1.5 and 2.0 K min^{-1} for the DSC 100 and 10 K min^{-1} for the DSC 200.

Procedure

A pair of aluminium sample containers with similar weights were chosen for the C_p measurements. The sapphire standard had a similar weight to that of the samples and all measurements were carried out using the same procedure: the temperature was held at 433 K for 3 min and the sample was scanned at various cooling rates to 313 K; after holding at 313 K for 3 min, it was scanned at the same rate to 433 K, and held for 3 min for each measurement. The calculation of C_p on both cooling and heating cycles was by the same method as reported previously [7,8]. Gas flow was prevented during measurement. Nine measurements were determined for each condition.

RESULTS AND DISCUSSION

In the DSC measurement, the output signal difference between the base line and the scan curve of the sample increased with increasing sample weight; however, the temperature distribution within the samples also increased [1]. Therefore, the sample weight influenced the precision of the C_p values [8]. The effect of sample weight on the reproducibility of the C_p values measured during the cooling and heating cycles is shown in Fig. 1. The relative standard deviation (RSD) of the value obtained for sapphire from the corresponding literature value at 373 K was used in Fig. 1 in order to confirm the reproducibility. The scan rate was 1 K min^{-1}. The reproducibility of the C_p values obtained on cooling and heating were almost the same, showing a minimum with 20 mg of sample weight.

Using 20 mg of sample, the C_p of sapphire was measured at various scan rates on cooling and heating. The relative standard deviation of the obtained C_p values from the corresponding literature value at 373 K is shown in Fig. 2 as a function of the scan rate. The experimental C_p values observed on cooling and heating correspond well with the literature values at scan rates ranging from 1.0 to 2.0 K min^{-1}. Because the output signal difference between the base line and the scan curve of the sample became small at low scan rates, the reproducibility of the observed C_p values was poor at 0.5 K min^{-1}.

In order to estimate the reproducibility of C_p values obtained, the C_p measurement of sapphire was carried out at 1.5 K min^{-1} in the temperature range 313–413 K on cooling and heating. The sample weight used was 20

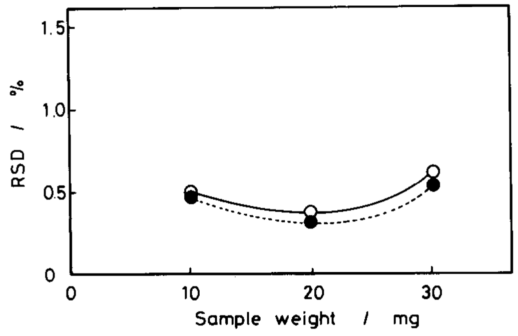

Fig. 1. Effect of sample weight on relative standard deviation (RSD) of the C_p values obtained for sapphire from the corresponding literature value at 373 K on cooling (o) and heating (●).

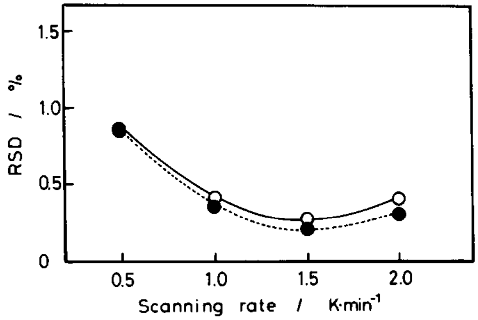

Fig. 2. Effect of scan rate on relative standard deviation (RSD) of the C_p values obtained for sapphire from the corresponding literature value at 373 K on cooling (o) and heating (●).

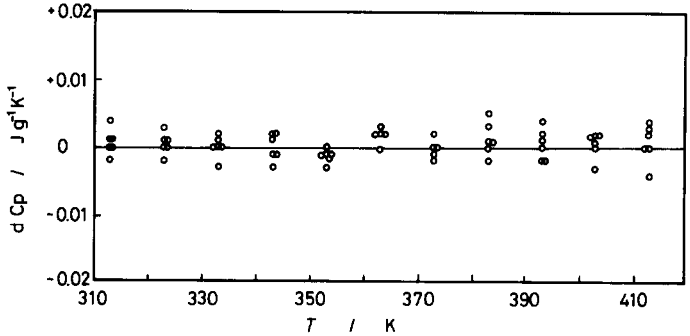

Fig. 3. Temperature dependence of the deviation of experimental C_p values of sapphire observed on heating from the corresponding literature values. The scan rate was 1.5 K $\min^{-1}$ and the sample weight was 20 mg.

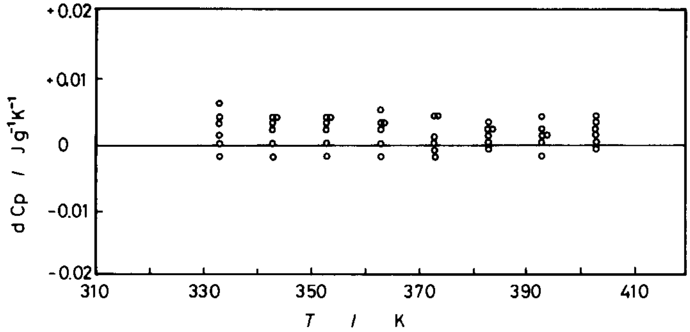

Fig. 4. Temperature dependence of the deviation of experimental C_p values of sapphire observed on cooling from the corresponding literature values. The scan rate was 1.5 K $\min^{-1}$ and the sample weight was 20 mg.

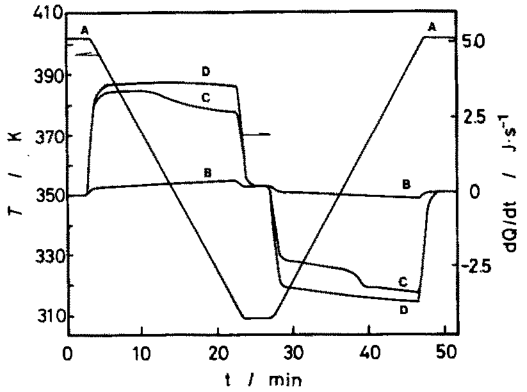

Fig. 5. DSC curves of C_p measurement for polystyrene on cooling and heating at 5 K min^{-1}. Temperature (A), DSC curves of empty sample container (B), polystyrene (C) and sapphire (D).

mg. Figures 3 and 4 show the difference between the experimental C_p values and the corresponding literature values at temperatures ranging from 313 to 413 K on heating and cooling, respectively. The experimental values obtained for six different scans were plotted in the figures. In the experimental temperature range, the relative standard deviation of the experimental C_p values from the corresponding literature value was within 0.5% on both cooling and heating.

Stacked DSC curves of the empty sample container, sapphire and polystyrene are shown in Fig. 5. The sample weight used was 20 and 30 mg for polystyrene and sapphire, respectively. The scan rate was 5 K min^{-1} which gave poor reproducibility among the scan rates used in this study. However, the three DSC curves are superimposed under isothermal conditions.

Figure 6 shows the experimental C_p values of polystyrene observed at 10 K min^{-1} both on heating and cooling. The C_p values observed on cooling

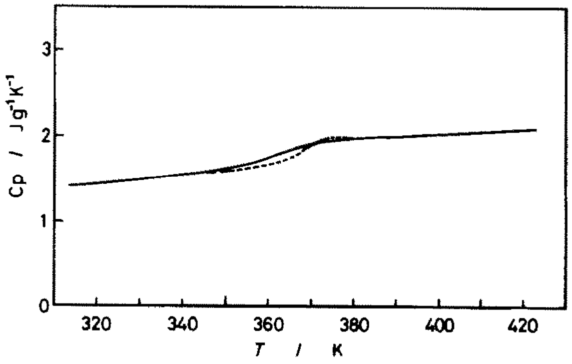

Fig. 6. C_p of polystyrene measured on cooling (solid line) and heating (dotted line) at 10 K min^{-1}.

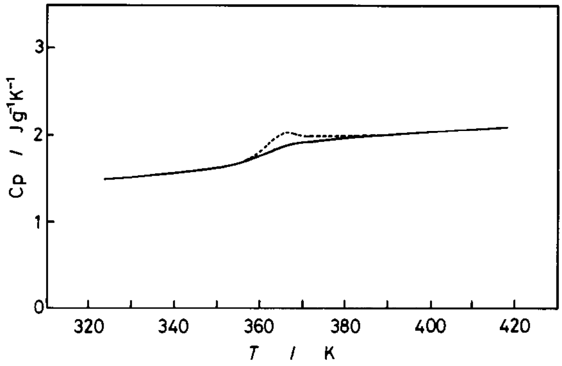

Fig. 7. C_p of polystyrene measured on cooling (solid line) and heating (dotted line) at 1.5 K min^{-1}.

agreed with the values observed on heating in the glassy state and the super-cooled liquid state. However, the C_p values in the glass transition region were different during cooling and heating, with the C_p values observed on heating being lower than those on cooling in the temperature range 340–370 K. The C_p curve on heating shows a small peak due to the enthalpy relaxation [10,11] in the glass transition region.

The C_p values of polystyrene observed at 1.5 K min^{-1} both on heating and cooling are shown in Fig. 7. As was seen for measurement at 10 K min^{-1}, the C_p values observed on cooling agreed with the values observed on heating in the glassy state and the super-cooled liquid state. However, the C_p values observed on heating were higher than values observed on cooling in the glass transition region. The endothermic C_p peak due to the enthalpy relaxation observed at 1.5 K min^{-1} on heating is larger than that at 10 K min^{-1}.

Comparing the C_p values on cooling at different scan rates, the C_p values observed at 1.5 K min^{-1} agree with those at 10 K min^{-1} over the complete experimental temperature range. This suggests that the freezing transitions of the super-cooled liquid state to the glassy state at different scan rates are almost the same in this scan rate range. Hutchinson and Kovacs reported that the specific volume changes at different cooling rates were explained by retardation kinetics using a single ordering parameter [12]. According to their cooling data, the volume change at 3 K min^{-1} differed from that at 0.6 K min^{-1} [10]. Although different cooling rates were used in the dilatometric and calorimetric studies, the enthalpy freezing process may differ from the volume freezing process.

The characteristic difference between the C_p changes measured at different scan rates appeared in the glass transition region on heating. The experimental C_p values observed at 1.5 K min^{-1} were larger than those at 10 K min^{-1} in the temperature range 350–375 K. The C_p values observed under both conditions were the same below 350 and above 375 K. As

TABLE 1

Characteristic temperatures (K) in the glass transition region of polystyrene

Scan rate ($K\ min^{-1}$)	T_{ig}^{C} (K)	T_{mg}^{C} (K)	T_{eg}^{C} (K)	T_{ig}^{H} (K)	T_{mg}^{H} (K)	T_{eg}^{H} (K)
1.5	369.3	362.2	354.4	356.9	360.9	373
10	370.1	362	351.9	363.9	367.6	380.4

described above, the C_p endothermic peaks were observed in the glass transition region. These phenomena are explained by the enthalpy relaxation caused by different annealing times at the glassy state. The sample prepared by cooling at 10 K min^{-1} had higher excess enthalpy than the sample prepared by cooling at 1.5 K min^{-1}.

It is well known that the glass transition is a relaxation phenomenon and that the glass transition temperature (T_g) depends on the thermal history of the sample and the scan rate. Various temperatures were used as the glass transition temperature (T_g) in the case of DSC measurements. The extrapolated onset temperature, the midpoint temperature and the extrapolated end temperature on cooling (T_{ig}^{C}, T_{mg}^{C}, T_{eg}^{C}) and on heating (T_{ig}^{H}, T_{mg}^{H}, T_{eg}^{H}) were determined according to the recommended method [9]. Here, superscripts C and H denoted cooling and heating processes, respectively. (Note, $T_{ig}^{C} > T_{mg}^{C} > T_{eg}^{C}$ and $T_{ig}^{H} < T_{mg}^{H} < T_{eg}^{H}$.) These temperatures are shown in Table 1. Despite the different scan rate, each characteristic temperature obtained from cooling C_p curves shows good agreement.

CONCLUSIONS

Heat flux DSC showed good precision and reproducibility of the C_p values measured on cooling and heating cycles at scan rates ranging from 1.5 to 2.0 K min^{-1}. The C_p values of polystyrene obtained on cooling and heating showed good agreement at both the glassy and the super-cooled liquid states. The C_p values of polystyrene obtained showed hysteresis in the glass transition region on cooling and heating. The magnitude of this hysteresis was smaller at 1.5 K min^{-1} than at 10 K min^{-1}.

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