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Dedicated to Professor Bernhard Wunderlich on the occasion of his 65th birthday

NON ISOTHERMAL HEAT CAPACITIES AND CHEMICAL REACTIONS USING A MODULATED DSC*

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Abstract

An evaluation of measurements of heat capacities by modulated differential scanning calorimetry, MDSC is presented. Heat capacities were obtained from 130 to 550 K by a non isothermal technique in which a periodic modulation was added to the linear heating rate. Effects of amplitude and period of modulation, sample weight, sample type, pan type, and cell imbalance are described. Results are compared with those obtained using the isothermal technique. Heat capacity could be measured well into the decomposition region and separated from the non reversing signal due to chemical reaction (degradation), thus allowing a precise detection of onsets of the thermal degradation. This additional information will aid in the interpretation of the degradation chemistry, a field vital for the petroleum-industry.

Keywords: conditions, degradation, heat capacity, liquid, MDSC, modulated DSC, solid

Introduction and theory

Modulated differential scanning calorimetry (MDSC), a new approach to thermal analysis was introduced as a commercialized technique at the NATAS meeting in 1992 [1]. There have been several publications in the literature describing its applications [2–4]. Heat capacity measurements under isothermal conditions using the MDSC have been reported [5] and a detailed description on the mathematical treatment is described [6]. In this paper, we describe the use of the non isothermal technique to obtain heat capacities using the MDSC. Measurements of precision heat capacities are important not only for obtaining the needed thermodynamic information, but also for gaining additional insight into the non equilibrium processes. These include events such as occurrence of a chemical reaction, e.g. oxidation associated with lubricants and fuels at high temperatures in an engine environment. The main advantage of the non isother-

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mal MDSC technique over standard DSC lies in the separation of any irreversible processes in the sample. Not only can the precise onset of oxidation be identified, but C_p can now be measured in the presence of oxidation with only minimal errors arising from the effects of permanent changes in composition and mass of the sample.

A brief mention of the theory is needed to lay the foundation of this paper. The mathematical description and details are described in Ref [6]. Heat capacity measurements by the quasi-isothermal technique [5] and the effect of modulation on the glass transition phenomenon are described [7]. The heat capacity measured by a conventional DSC under conditions of negligible temperature gradient within the sample is in reasonable approximation given by the equation [8]:

$$C_P = K\ \Delta T/q = K'\Delta H_f/q \tag{1}$$

where ΔT is the temperature difference between reference and sample, K is a temperature dependent constant, q is the linear heating rate, ΔH_f is the differential heat flow into or out of the sample and reference. Both ΔT and ΔH_f are proportional to the heating rate. Therefore, in order to get high precision one has to use a high heating rate. In MDSC, the block temperature $T_b(t)$ is modulated with a sinusoidally changing amplitude. This produces a corresponding modulation on the sample and the reference temperatures. The block, sample and the reference temperatures [$T_b(t)$, $T_s(t)$ and $T_r(t)$ respectively] are given by the following equations [6]:

$$T_b(t) = T_o + qt + A_{T_b} \sin(\omega t) \tag{2}$$

$$T_s(t) = T_o + qt - (qC_s)/K + A_{T_s} \sin(\omega t - \varepsilon) \tag{3}$$

$$T_r(t) = T_o + qt - (qC_r)/K + A_{T_r} \sin(\omega t - \Phi) \tag{4}$$

T_o is the initial temperature, q is the underlying heating rate and A_T is the amplitude of modulation (where subscripts b, s, and r refer to block, sample and reference). Sample and reference heat capacities are given by C_s and C_r and K is the Newton's Law constant. ω is the frequency of modulation ($\omega = 2\pi/p$, p is the period of oscillation), and ε and Φ are the phase angles between block and sample and reference temperature. Actual heating and cooling of the sample can then be described by the equation:

$$\mathrm{d}T_s(t)/\mathrm{d}t = q + A_{T_s}\,\omega \cos(\omega t - \varepsilon) \tag{5}$$

At constant ω and fixed reference, the heat capacity obtained by the non isothermal technique is given by the simplified equation:

$$C_P = K_c\,(A_{H_f}/A_{T_s})\,/\omega \tag{6}$$

where K_c is the calibration constant for the cell (obtained by measuring the C_p of a sapphire standard at the chosen frequency), and A_{H_f} is the amplitude of heat flow. In MDSC, the precision of C_p measurements is achieved through modulation where the maximum heating and cooling rates caused by modulation are given by $A_{T_s}\omega$.

This paper describes the importance of calibrations needed for the heat capacity measurements by the non isothermal technique. This technique has a major advantage over the conventional DSC as it can eliminate irreversible processes in the sample and any slow drifts of the baseline of the calorimeter due to heat losses or gains. The application of the MDSC in separation of the non reversing component from the heat capacity during thermo-oxidative degradation will also be described. Similar applications have also been given earlier [1–4]. Even though the non reversing component contains, in addition to the kinetic information on degradation, additional contributions due to effects of heat loss [3], it is an improvement over data obtained from a conventional DSC alone. The slow reactions can now be followed without disturbance from contributions arising from the heat capacity as long as the mass losses or chemical changes are small.

Experimental

A TA Instruments Inc., modulated DSC (MDSC) 2910, equipped with a 2100 thermal analysis system was used for heat capacity measurements from 130 to 550 K. An auto-fill liquid nitrogen cooling accessory was attached to cool to sub-ambient temperature and an auto sampler was used to place the sample and reference pans on the cell platforms to eliminate errors arising due to positioning. A nitrogen gas flow of 50 cm^3 min^{-1} was used as a purge gas. The temperature calibration was carried out with four standards (cyclohexane, indium, tin and naphthalene). The baseline slope was corrected using the calibration procedure described in the instrument manual. The MDSC cell constant was left at the factory setting of 1 so that this could be evaluated with respect to the various parameters described below.

Experiments were carried out with different weights of sapphire powder (6–45 mg) and a sapphire disc (≈61 mg) for calibration. The data obtained with the MDSC under conditions described below were compared for accuracy with the standard heat capacities of sapphire [9]. Heat capacity was also evaluated for polystyrene, aluminum, and quartz as standards. Sample masses for these ranged between 20–30 mg. Measurements were made, both, in encapsulated and hermetically sealed aluminum pans to study the effect of pan shape on heat capacity both for solids and for liquids. Unless specified, the data reported were obtained in encapsulated aluminum pans. Liquid samples evaluated included water, hexadecane, and an ester-based lubricant oil. In all experiments, care was taken to ensure that the samples had achieved a steady state prior to heating. Unless specified, all data reported were obtained with a cell having an imbalance of 1.6 mJ/°C. The variables investigated with a sapphire disc as a standard are listed below:

(1) Effect of period: The cell constant, K_c, was determined using a heating rate of 5°C $\min^{-1}$, modulation amplitude of 1°C and varying the period of modulation from 40 to 90 seconds;

(2) Effect of amplitude: With a period of 80 seconds and a heating rate of 5°C $\min^{-1}$, K_c was obtained at amplitudes ranging between 0.2 to 5°C;

(3) Effect of different cells: K_c for a sapphire standard was evaluated for three different MDSC cells using a period of 80 seconds, amplitude 1°C and a heating rate 5°C $\min^{-1}$. The three cells used had an imbalance of 0.8, 1.6 and 4.4 mJ/°C, respectively. This imbalance is the heat capacity in mJ/°C that was recorded using an empty calorimeter (without aluminum pans) by carrying out an MDSC experiment from –150 to 300°C with a period of 80 seconds and an amplitude of 1°C together with a heating rate of 5°C $\min^{-1}$. The values of imbalance listed above are the maximum values for the full temperature range. This experiment was conducted to investigate whether a single MDSC experiment is sufficient to obtain heat capacity of a sufficient precision, or if a baseline subtraction needs to be performed for each sample run, as is usually done in a conventional DSC, or if in addition to the baseline subtraction, the cell platforms for the reference and the sample positions need to be balanced by adjusting empty pan weights till the cell shows a negligible imbalance.

Study of thermo-oxidative degradation

Degradation reactions were investigated in low molecular weight additives and mineral oil base stocks (typical molecular weights were less than 10.000). The sample was sealed in air in a hermetic pan and heated at 5°C $\min^{-1}$, using a period of 80 seconds and an amplitude of 1°C from room temperature to 300°C. The non reversing component arising due to the thermo-oxidative degradation was separated from the reversing heat capacity using the MDSC software.

Results

Effect of period of modulation

The effect of varying the period of modulation on the heat capacities of a sapphire disc (≈61 mg) is shown in Fig.1. The MDSC cell constant, K_c, obtained as a ratio of $C_{p(\mathrm{literature})}/C_{p(\mathrm{experimental})}$ of a sapphire standard, shows a strong

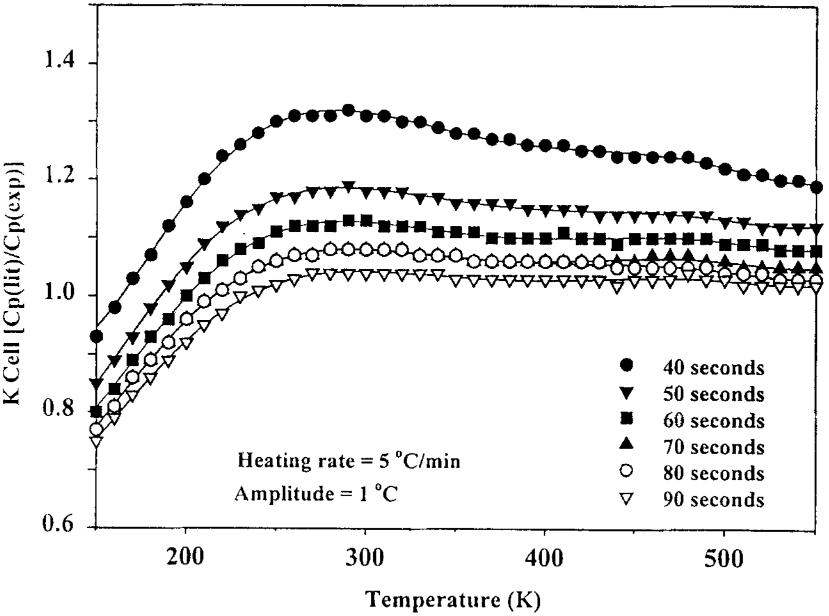

Fig. 1 Variation of cell constant, K_c obtained from heat capacities of a sapphire disc (≈ 61 mg) [C_p(literature)/C_p(experimental)], with change in period of modulation from 40–90 seconds. The amplitude of modulation and the underlying heating rate were fixed at 1°C and 5°C min^{-1}, respectively

dependence on the period p, as was also reported for C_p obtained from the isothermal experiments [5] and is expected from the mathematical description of MDSC [6]. The measured heat capacities for sapphire at a period of 90 seconds were close to the literature data (K_c ranged between 1.02 and 1.04 from 250 K to 570 K). Lower periods showed larger deviations of standard heat capacities from the measurements. These deviations become even more obvious at temperatures below 300 K. Not only is K_c dependent on the period, but it also changes with temperature for a given period. It is clear from this experiment that a single value of cell constant cannot be used for correction of the measured heat capacity data of samples as this would give errors as high as 15–20%. With a change in temperature, the ratio of heat carried from block to sample and reference by conduction and radiation changes and this results in a change in K_c with temperature. Therefore, in order to make a selection of the right value of a modulation period, its variation over the entire temperature range was considered. Since values of K_c at about 70 and 80 seconds were relatively close at higher temperatures, a period of 80 seconds was chosen for measurements as larger period gave slightly better values for the cell constant a low temperature. A period of 90 seconds would have been an even better choice as longer periods allow better thermal equilibration of the sample, but this was avoided as the measurements would have then been close to the upper limit of the instrument.

Effect of amplitude of modulation

Changing the amplitude from 0.2 to 5°C has little effect on the heat capacity of the sapphire standard (Fig. 2). Considerably larger amplitudes could be used with liquid nitrogen as a coolant and no sine wave distortion of the heat flow during modulation could be observed even at an amplitude of 5°C. The maximum achievable amplitude at a heating rate of 5°C min^{-1} when the sample will only be heated and not cooled with a 80 seconds period is 1.06°C [given by the equation [amplitude =(heating rate)×(period)/(2π×60 seconds)]. Since precision of the measurements did not seem to change with amplitude, a value of 1 °C was selected to avoid cooling of the sample during the measurement.

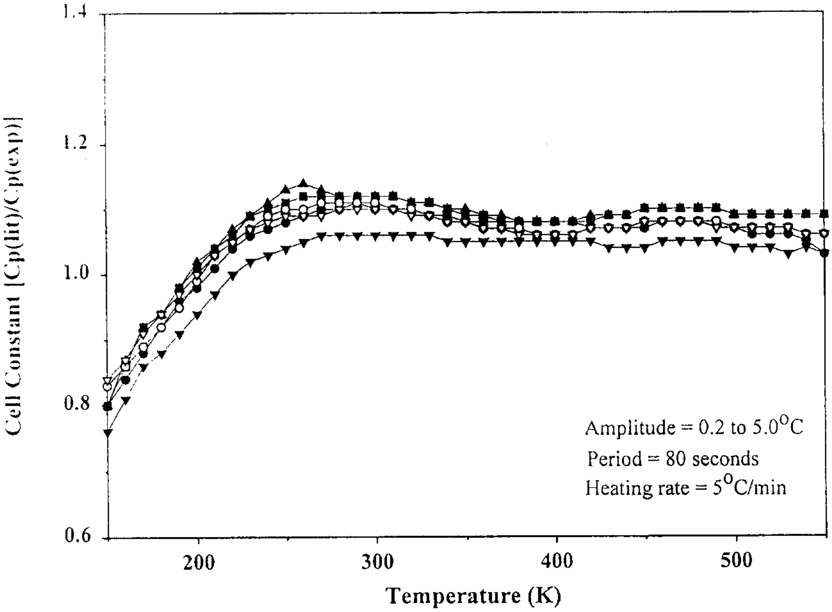

Fig. 2 Variation of the cell constant K_c, for a sapphire disc (≈61 mg) with change in amplitude from 0.2 to 5°C. The period of modulation was 80 seconds and the underlying heating rate was 5°C min^{-1}

Effect of cell imbalance

The effect of cell imbalance for three different MDSC cells on K_c was also measured (Fig. 3). From 140 to 550 K, the cell constants for a sapphire standard for the three different cells were as follows: cell imbalance of 4.4 mJ/°C, K_c ranged between 0.71–0.98; cell imbalance of 1.6 mJ/°C, K_c was 0.74–1.03; and for a cell with an imbalance of 0.8 mJ/°C, K_c was 0.81–1.10. Thus, a cell in which both reference and sample platforms are not balanced in terms of thermal response affects the calibration data. The cell imbalances reported above were obtained by measuring the heat capacity with an empty cell (no aluminum

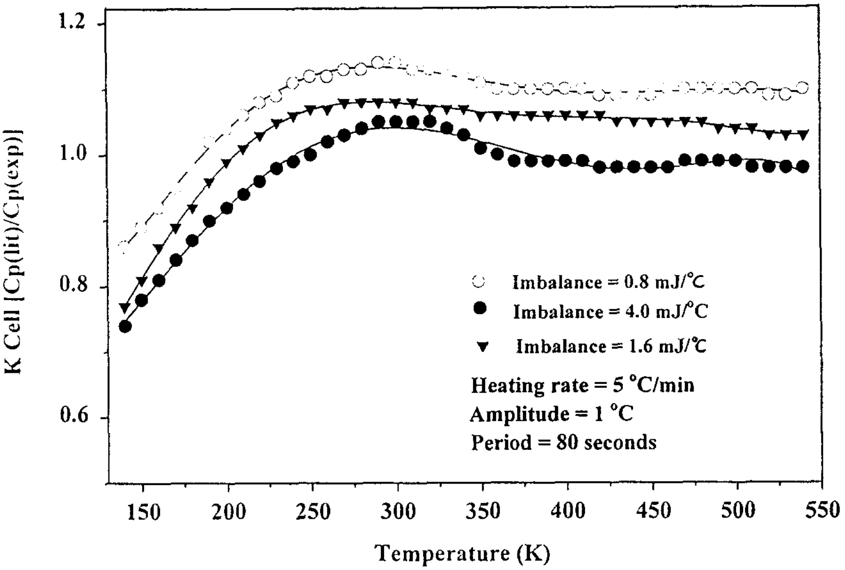

Fig. 3 Change in cell constant, K_c, for a sapphire disc obtained on three different cells having an imbalance of 0.8, 1.6 and 4.4 mJ/°C. For modulation of the linear underlying heating rate of 5°C $\min^{-1}$, a period = 80 seconds, and an amplitude of 1°C were used

pans). An example of its effect on data for standards is the heat capacity data for polystyrene standard. The C_p obtained with a cell with highest imbalance (4.4 mJ/°C) after correction with the cell constant of a sapphire standard were higher by about 5–7% (from 300 to 500 K) than the literature values while those with an imbalance of 0.8 mJ/°C were within 1–2% for the same temperature range. Measured C_p data from a cell with a large imbalance, therefore, needs to be corrected by baseline subtraction of C_p obtained using empty aluminum pans of matching pans weights. This leads to an added step in getting direct heat capacities from an MDSC, but needs to be done in case a cell has a large imbalance.

Heat capacities for standards

The heat capacities for polystyrene and quartz were obtained from 140 to 550 K using a cell with the least imbalance (0.8 mJ/°C) and are given in Table 1. As pointed out in the above paragraph, the baseline was not subtracted for these data. The precision of the heat capacities above 240 K was quite good, showing that the non-isothermal method can be used to obtain good data after proper calibration beyond this temperature. These measurements can be compared to the data from the MDSC obtained using the quasi-isothermal method where the precision is expected to be better than 1%. The errors for the C_p data for polystyrene obtained using an isothermal method (period =60 seconds and amplitude of 0.5°C) and the same cell as was used for the non isothermal meas-

Table 1 Heat capacities from an MDSC for various standards

T/K	K_c, Sapphire ($C_{p\,\mathrm{lit}}/C_{p\,\mathrm{exp}}$)	Polystyrene C_p Error/%	Quartz C_p Error/%
140	0.82	11.3	–
160	0.88	9.8	–
180	0.95	8.9	10.9
200	1.01	7.6	9.3
220	1.06	6.1	7.3
240	1.09	4.4	5.0
260	1.11	3.2	3.1
280	1.13	0.1	1.6
300	1.14	-1.3	0.1
320	1.13	2.5	-0.9
340	1.12	2.5	-1.7
360	1.11	2.5	-1.9
380	1.10	2.3	1.8
400	1.10	2.3	0.5
420	1.10	1.6	1.6
440	1.09	1.2	2.3
460	1.09	1.0	1.0
480	1.10	0.7	-0.7
500	1.10	0.7	0.2
520	1.10	0.4	0.9
540	1.09	0.9	-0.5

The RMS error of heat capacities from 320 to 550 K was 1.4±0.8% for polystyrene and 0.02±1.5% for quartz.

urements reported in this paper were as follows; at 320 K, -2.1%; 340 K, -1.1%; 360 K, -0.9%; 380 K, -0.3%; 400 K, -0.6%; 420 K, -0.1%; 440 K, -0.8%; 460 K, -0.3% and 480 K, -0.6%. The advantage of the non isothermal method lies in the fact that measurements can be made continuously through the transition regions and in a shorter time. The larger errors below 240 K are most likely due to the dynamic nature of the experiment. The period and amplitude of modulation seem to need at least 15–20 minutes to stabilize after the start of the experiment.

Effect of sample mass, sample conductivity and pan type on heat capacity

The effect of varying sample mass of powdered sapphire in encapsulated aluminum pans is shown in Fig. 4. Higher sample mass causes lower measured

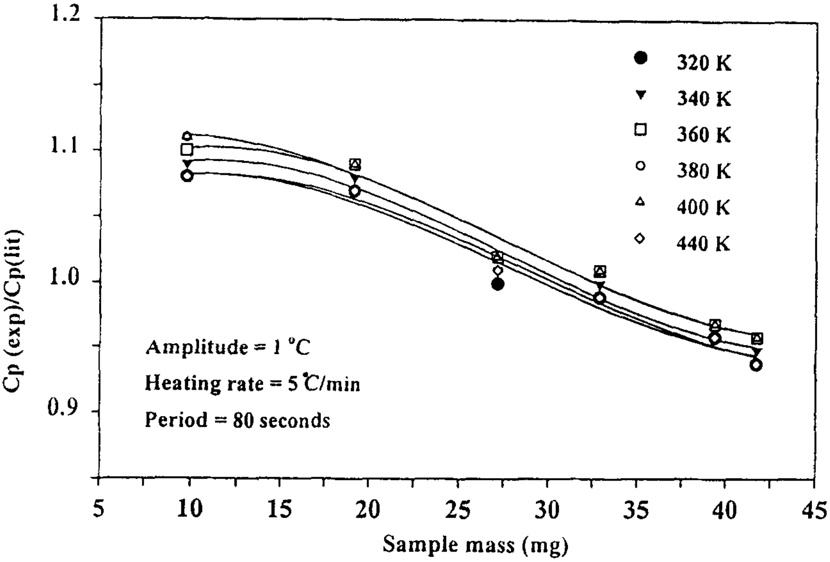

Fig. 4 Experimental heat capacities of sapphire powder of varying sample mass evaluated using encapsulated aluminum pans using a heating rate of 5°C min^{-1}, period =80 seconds and an amplitude of 1°C

heat capacity for sapphire powder beyond about 20 mg. For these measurements a cell with an imbalance of 1.6 mJ/°C was used and no baseline subtraction was performed for the heat capacities reported. This variation of C_p with sample mass was rather surprising, especially since it has been reported that C_p for sapphire powder obtained with quasi-isothermal measurements does not depend on sample mass up to about 50 mg [5]. Large sample mass is expected to cause insufficient thermal diffusivity and heat capacity measurements using an MDSC should, therefore, be restricted to small sample masses (less than 15 mg).

In a MDSC it is not only the mass of the sample that affects the heat capacities, but the sample type is equally important. The heat capacities for molded films of PVC were measured from 300 to 370 K for samples weighing between 1.5 and 10 mg using the same cell and similar modulation conditions as above (period = 80 seconds, amplitude =1°C and heating rate =5°C min^{-1}). The data clearly show that for a good precision and repeatability, it is necessary to have good thermal contact with the sample pan. The variation in sample mass did not affect the heat capacities, thus indicating that using a small size sample that provides a good contact with the pan base are important variables.

Similarly, heat capacities were also evatuated for a synthetic lubricant oil from 300 to 370 K, using the same conditions for modulation as used above for powder and film samples. The mass of the sample was varied from 4.5 to 18 mg. The standard literature data could be reproduced to an accuracy of about 1–2% for all the samples. These results indicate that for a liquid sample effect of mass is not significant at least up to about 18 mg. But it is always helpful to establish a weight dependency for samples with poor conductivity.

Heat capacities in a hermetic pan

Every effort to measure heat capacities of liquids in a hermetically sealed aluminum pan was unsuccessful. The present shape of the pans does not allow measurements to be made using a MDSC. Example of some results are shown in Table 2. These data were obtained in pans with a flattened lid to improve the contact with the sample. The heat capacities for sapphire were lower than those obtained in an encapsulated pan (the cell constant, 'K_c' given in Table 2 was higher than that given in Table 1). The data for some of the liquid samples clearly suggest that the present shape of the pan does not support C_p measurements by the MDSC technique.

Table 2 Heat capacities of various liquids using hermetic pans

T/K	K_c, Sapphire ($C_{p\,\mathrm{lit}}/C_{p\,\mathrm{exp}}$)	Water C_p Error/%	Heptadecane C_p Error/%	Lube oil C_p Error/%
310	1.44	6.3	–5.4	–13.1
320	1.43	6.2	–3.2	–13.6
330	1.42	8.6	–4.9	–13.8
340	1.41	3.6	–6.1	–13.7
350	1.40	3.0	–6.5	–13.2
360	1.39	–	–7.3	–12.6

Chemical reactions

Figure 5 shows the separation of the non reversing and the reversing heat capacities for a proprietary additive used in lubricants. It is possible to precisely identify the onset of small amounts of a reaction that occurs in this sample. The importance lies in the measurement of heat capacity through this reaction which is believed to be a thermo-oxidative degradation reaction. The stability of the additive can be thus measured to more than 100 K beyond the beginning of the exothermic peak. The C_p data obtained in this region were compared with the heat capacities from the ATHAS data bank [10]. The typical errors between the measurements and the literature data were less than 3%. Figure 6 shows the traces for a series of ethylene-based copolymers with varying compositions. The extent of reaction changes with the comonomer content and the transition shifts to higher temperature. These measurements are being used to provide an insight into the role of composition on the stability at high temperatures.

Discussion

The results clearly show that it is possible to use to the MDSC for measurement of heat capacities after proper calibrations of the instrument and by using the right combination of modulation conditions. Careful choice of the run parameters is, however, necessary. Figures 1–3 illustrate the effect of various con-

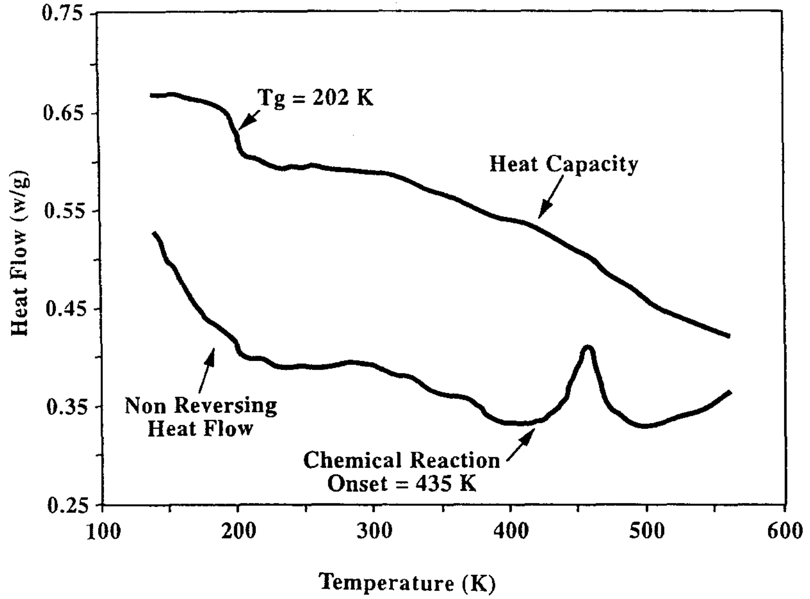

Fig. 5 Separation of non reversing signal showing a chemical reaction (thermo-oxidative degradation) in an additive. Heat capacity (reversing signal) obtained through the reaction region

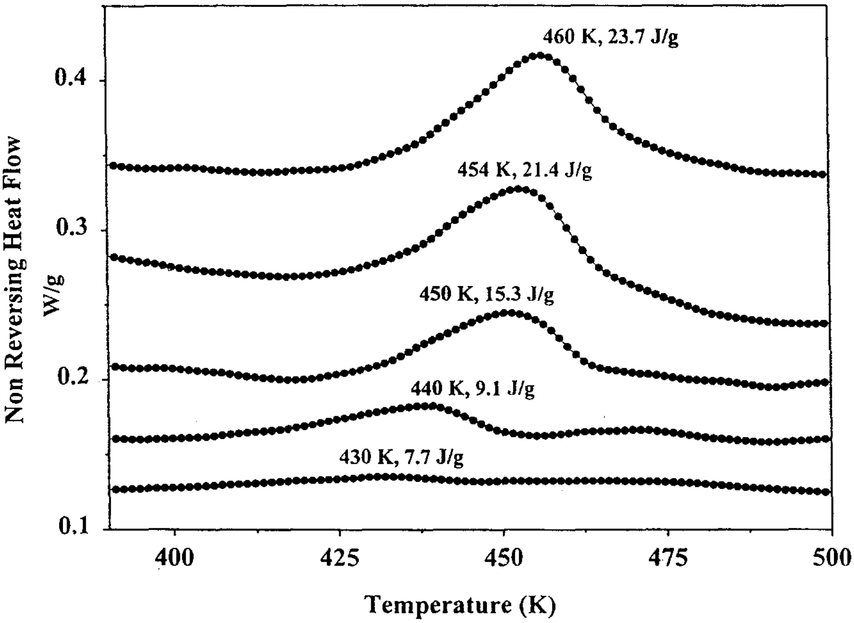

Fig. 6 Extent of high temperature reaction explored using the non reversing signal from an MDSC in a series of copolymers with varying compositions. Period =80 seconds, amplitude = 1°C and heating rate = 5°C min^{-1}

ditions and the choice of best conditions. The continuously changing calibration constant, K_c, points to the impossibility of using a one-point calibration. Having identified the limitations (Fig. 4 and Tables 1 and 2), it is then relatively easy to stay safe within the limits of the parameters.

The calibration constant K_c obtained for the non isothermal measurements increases with frequency (frequency, $\omega = 2\pi/p$). A similar dependence was also observed for the quasi-isothermal experiments, where in addition, the frequency dependence of K_c for the quasi-isothermal measurements of heat capacities was shown to follow the equation given below [5]:

$$K_c = C_p \text{ (literature) } / \, mc_p \sqrt{1 + (C'\omega/K)^2} \tag{7}$$

where 'm' is the mass and 'c_p' is the experimental specific heat capacity of the sapphire sample; C' is the heat capacity of the empty pan, and K a constant. For the non-isothermal measurements this equation was also applied. The constant

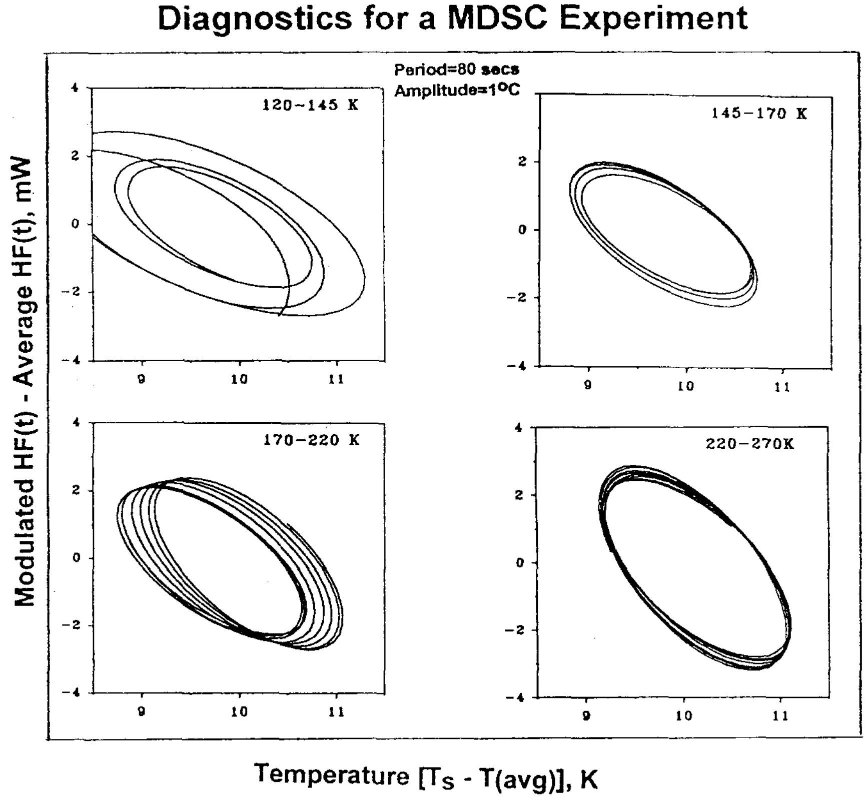

Fig. 7 Diagnostics for a non isothermal MDSC experiment using Lissajous figures. The curves show the changes in heat flow minus average heat flow followed in a heating experiment. The experimental conditions for a sapphire disc of ≈61mg mass with period =80 seconds, amplitude =1°C, and the underlying heating rate =5°C min^{-1}

K_c at each temperature was evaluated as a function of ω ($\omega = 2\pi/p$ and p was varied from 40 to 90 seconds as shown in Fig. 1). As examples, the regression analysis at six different temperatures is shown. The values of C_p(literature)/mc_p at 400 K, 350 K, 300 K, 250 K and 200 K were 0.969 (R^2 = 0.99), 0.962 (R^2 = 0.99), 0.966 (R^2 =0.99), 0.944 (R^2= 0.99) and 0.86 (R^2=0.99) respectively. It was expected that since the steady state is not maintained through the experiment especially at the low temperatures (below 250 K), Eq. [7] could not be fully applied to the non isothermal experiments.

A diagnostic check for the maintenance of steady state in the MDSC experiment as described in [5b and 6] was adopted also for the non isothermal data described in this paper. As long as the MDSC is in steady state a plot of heat flow *vs.* modulated temperature should give an elliptic Lissajous figure. A typical example from the calibration data for sapphire from 120 to 470 K is given in Figs 7 and 8. The plots of the modulated heat flow *HF*(*t*) *vs.* the modulated temperature, $T_s(t)$ were obtained by separating the non isothermal experiment into several shorter temperature ranges and the nature of ellipse generated is used to detect whether the sample during measurement was in steady state or

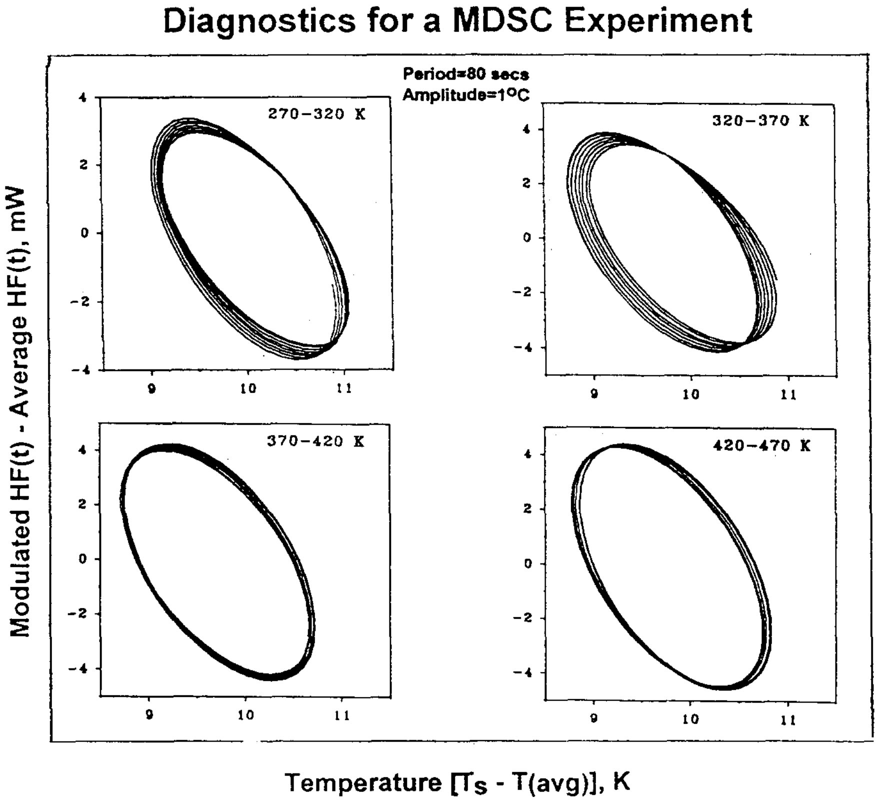

Fig. 8 Similar plots as in Fig. 7 for higher temperature ranges. Note: both Figs 7 and 8 are plots of a single experiment

not. These results help to explain some of the large deviations that we see in K_c at low temperature and also in the low temperature heat capacities given in Table 1. For a good measurement, the ellipse should be symmetrically centered (about 0 on the Y axis and 10 on the X axis) and not show any significant distortions. At low temperatures (below 145 K) not only is the ellipse asymmetric but it is also not centered. This is also true up to about 220 K, beyond which the performance improves. The data in Table 1 also increase in precision beyond this temperature, indicating thus that the poor quality of the data at low temperatures arises from the sample deviating from steady state. So long as the ellipse shifts as a whole, as indicated in Fig. 8 (temperature range 370 to 420 K), the C_p output will show only negligible effect since the axis ratio alone is used for the computation of C_p [Eq. (6)].

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