

## **TEMPERATURE MODULATED DSC FOR THE INVESTIGATION OF POLYMER MATERIALS**

### **A brief account of recent studies**

*M. Ribeiro and J.-P. E. Grolier*

Laboratoire de Thermodynamique et Génie Chimique (UPRES A CNRS 6003) Université Blaise Pascal, 63177 Aubière, France

### **Abstract**

Temperature modulated differential scanning calorimetry (TMDSC), the most recent development that adds periodic modulation to the conventional DSC, has recently seen a fast growth due to availability of commercial instrumentation. The use of the technique necessitates a total control of all of the experimental parameters. The papers focuses on recent applications to investigate polymers [1].

**Keywords:** calibration, glass transition, heat capacity, non-reversing heat flow, polymer, reversing heat flow, temperature modulated DSC

### **Introduction**

Temperature modulated differential scanning calorimetry (TMDSC) is now recognized as a very powerful analytical technique in pharmaceutical and food applications [2–5]; for example, to determine the purity of crystalline forms or to localize glass transitions. The technique, however, has been intensively used to investigate polymers. This paper reviews some particular aspects or advantages of using TMDSC for characterizing polymer materials; it has to be seen as a note providing advice and recommendation to properly use this technique.

In the last thirty years, the precision and the resolution of calorimetric methods such as AC-Calorimetry (alternating-current calorimetry), introduced by Sullivan and Seidel in 1968 [6], have increased significantly. The first real measurements of the so-called ‘modulated method’ have been obtained by Corbino in 1910 [7]; he showed how to use the resistance of an electrically conducting sample to determine the oscillation of the temperature. His technique, called ‘ $3\omega$  method’, was based on the thermal diffusion in a sample, using a metallic film to simultaneously induce the heating and detect the temperature.

The difference that allows to distinguish between ‘modulated temperature’ methods comes from the form of energy applied to impose the perturbation of the temperature; the modulation can be generated for example, by Joule effect [8], through light [9] or by electron bombardment [10].

The rapid evolution of both methodology and technology has led to recent applications of modulated temperature calorimetry, particularly the combination of the

technique with differential scanning calorimetry [11] to yield a commercial line of instruments (TMDSC for example, in the case of TA Instruments). Different terms such as 'periodic', 'oscillating', 'dynamic' or 'alternating' have thus been used to describe similar techniques based on different types of instruments.

The use of temperature modulated DSC to characterize polymers deals mostly with detection of weak transitions, determination of heat capacities in quasi-isothermal mode and separation of superimposed phenomena. We report here some recent results obtained when investigating samples of medium density polyethylene (MDPE) and of polystyrene (PS).

### Brief description of the technique

The mathematical development necessary to describe the technique is well known [11] and different approaches have been proposed [12].

The total differential heat flow obtained after deconvolution of the modulated heat flow represents the sum of two distinguishable contributions, because the response to the imposed temperature modulation is different depending on the phenomena submitted to the temperature changes. One component, called reversing heat flow, is linked to the heat capacity change; the modifications that depend on the temperature scanning rate can be cycled by alternating heating and cooling effects. The second component is linked to the kinetics and is called non-reversing heat flow, by opposition to the first one; modifications appearing in this signal depend only on the temperature.

The specific heat capacity  $c_p$  measured with a conventional DSC, under the conditions of negligible temperature gradient within the sample, is approximately proportional to the temperature difference between the sample and the reference or to the heat flow difference. Calculation of the sample heat capacity is possible through calibration data, at the working temperature, via the following relation:

$$mc_p = m_{\text{Al}_2\text{O}_3} c_{p(\text{Al}_2\text{O}_3)} \frac{a_s - a_b}{a_c - a_b} \quad (1)$$

where  $m$  is the mass of material and the quantities  $a$  represent the amplitudes of the heat flow (or temperature) differences signals for different situations corresponding to: sample, calibration and baseline runs designated respectively by 's', 'c' and 'b'. Usually, the baseline run ( $a_b$ ) is obtained with two empty aluminium pans. In a measuring run ( $a_s$ ), the sample is in one of the aluminium pans, whereas in the calibration run ( $a_c$ ) the sample is replaced by the standard sapphire ( $\text{Al}_2\text{O}_3$ ), having a well known specific heat capacity [13].

In the case of TMDSC the calibration equation takes the form [14]

$$(C_s - C_r) = \frac{A_\Delta}{A_{T_s}} \sqrt{(K/\omega)^2 + C_r^2} \quad (2)$$

where  $C_s$  and  $C_r$  represent the heat capacities of the sample and of the reference respectively (these quantities include the contribution of the sample and of the pans

which can be regarded as identical on the two sides),  $A_{\Delta}$  is the temperature difference amplitude between sample and reference,  $A_{T_s}$  the sample temperature amplitude (in Kelvin) and  $\omega$  designates the modulation frequency ( $=2\pi/p$  with  $p$  being the modulation period in s).  $K$  is the temperature-dependent Newton's law constant.

When calibrating with sapphire, Eq. (2) leads to the following equation:

$$(C_s - C_r) = K_{Cp} \frac{A_{HF}}{\omega A_{T_s}} \quad (3)$$

where  $A_{HF}$  refers to the amplitude of the differential heat flow, and  $K_{Cp}$  is the calibration constant for heat capacity measurements.

The heat capacity of the sample obtained using Eq. (3) allows the determination of the contributions of the reversing and of the non-reversing heat flows respectively, noted  $HF_{rev}$  and  $HF_{non-rev}$ , to the total heat flow  $HF_{tot}$  using the following relations:

$HF_{rev}$  signal = average temperature scanning rate  $\times$  heat capacity signal (conventionally, on heating a negative sign is necessary because an endothermic effect in the sample, i.e. heat consumption, creates a negative  $\Delta T$  between the sample and the reference).

$$HF_{non-rev} \text{ signal} = HF_{tot} \text{ signal} - HF_{rev} \text{ signal}$$

## Experimental

### *Instruments*

Two thermal analyzers were used for the present investigation. A temperature modulated differential scanning calorimeter TMDSC 2920 from TA Instruments. A refrigerated cooling system (RCS) provided with the instrument was used to cool the measuring system and operate it in the range 200–620 K. Argon from RCS was circulated ( $120 \text{ ml min}^{-1}$ ) in the cooling head. An argon flow ( $35 \text{ ml min}^{-1}$ ) was also used to purge the cell. The other instrument was a DSC 821 from Mettler-Toledo, capable of modulation, equipped with an auto-sampler changer. Dry nitrogen flow was also used to purge the cell; a gas flow of  $10 \text{ ml min}^{-1}$  was monitored and adjusted with a gas controller. Liquid nitrogen was used for the cooling system.

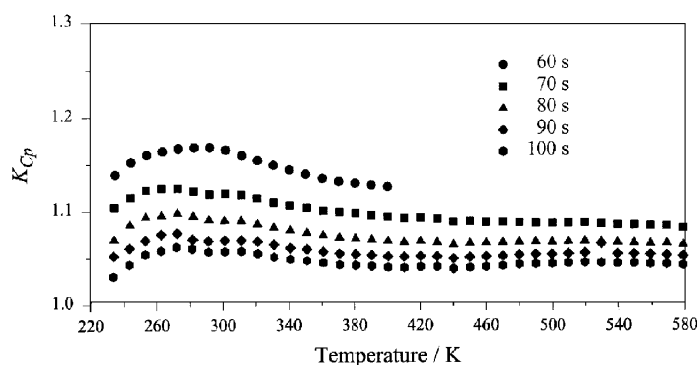
### *Materials*

The experiments were carried out with a sample of medium density polyethylene (MDPE) of about 55% crystallinity, provided by the Institut Français du Pétrole (I.F.P.) in the form of films ( $\sim 0.2 \text{ mm}$  thickness); this polymer had a number-average molecular mass  $M_n=11460$  and a mass-average molecular mass  $M_w=68500$ . The polystyrene (PS) sample, of the atactic type with  $M_n=111000$  and  $M_w=260000$ , was provided by Scientific Polymer Products, in the form of pellets. In order to calibrate the instruments for heat capacity, a sapphire disc of 22.160 mg was used. With the two instruments, DSC 2920 and DSC 821, the temperature calibration was based on 3 standard points, water (273.15 K) indium (429.75 K) and tin (505.08 K).

## Results and discussion

### *Assessment of experimental parameters*

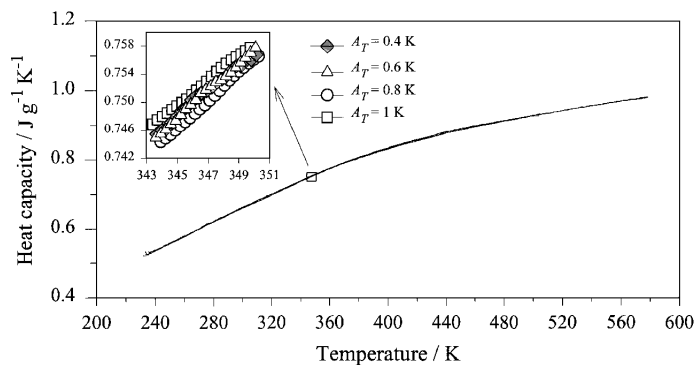
To fully control the technique, different aspects of the method have to be taken into account. Like DSC, TMDSC must be calibrated for temperature and heat with standard materials, usually metals due to their good thermal conductivity. For heat capacity calibration, it is common to use sapphire to obtain the constant  $K_{Cp}$ . It is primordial to determine this constant with good precision, non only to calculate the heat capacity of the sample but also to separate correctly the two contributions to the total differential heat flow.



**Fig. 1** Temperature dependence of the heat capacity constant  $K_{Cp}$  when the period varies from 60 to 100 s, with a fixed modulation amplitude of 1 K. Measurements were taken with the TA TMDSC 2920

Equations (2) and (3) evidently show that  $K_{Cp}$  must depend on the frequency of modulation  $\omega$  and thus on the corresponding period  $p$ . This period dependency is clearly seen on Fig. 1, in the case of quasi-isothermal mode (for which the average temperature scanning rate is zero), using the DSC 2920. For the experiments reported on this figure, the amplitude of modulation was 1 K and the period varying between 60 s and 100 s; each point represents the average of the last 10 min of a 20 min run, to be sure that equilibrium has been reached. As a matter of fact, a higher period requires a shorter time to reach equilibrium. For an experiment performed with a period of 30 s, the time necessary to achieve the equilibrium is 8 min whereas with a period of 50 s, this time is reduced to 6 min. These results are in good agreement with those reported by Varma-Nair *et al.* [15], in the case of a non-linear ramp of temperature (i.e. in a non-isothermal mode). The shape of the  $K_{Cp}$ -curves reflects the temperature dependence of  $K_{Cp}$  due to the variation of the heat exchange between the block on the one side and the sample and the reference on the other side.

Remarkably, the constant of calibration for heat capacity does not depend on the second parameter of modulation, the amplitude of temperature  $A_T$ , as it is shown on Fig. 2. In the example given on Fig. 2 the period has a fixed value, 60 s, whereas the amplitude  $A_T$  varies from 0.4 to 1 K. However, these results clearly indicate that  $K_{Cp}$

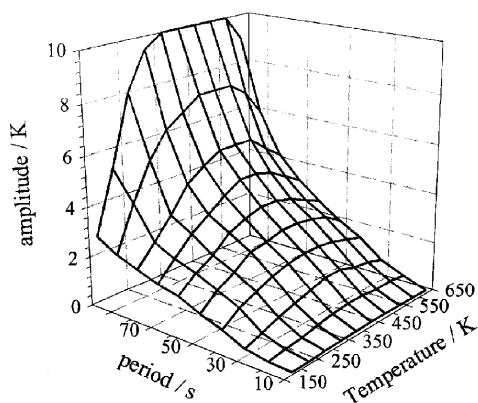


**Fig. 2** Variation of the heat capacity of sapphire when the amplitude varies from 0.4 K to 1 K, with a modulation period of 60 s. Measurements were taken with the TA TMDSC 2920. The enlarged section shows that four different runs are overlapping

has to be determined for each period of modulation and this, over the whole investigated temperature range.

The choice of the amplitude of modulation depends on the sample studied.  $A_T$  has to be sufficiently high to increase the sensitivity of the signal but not too much in order to allow the sample to follow the imposed perturbation. The period of modulation has to be higher than the relaxation time of the sample to allow the 'absorption of the modulation and its immediate restitution' and, obviously, higher than the time constant of the instrument used. Moreover, in order to separate precisely the two components, reversing and non-reversing heat flows, it is also necessary to perform 5 to 6 modulations during the studied transition, in order to apply Fourier transform calculations to the modulated signal.

The choice of the amplitude and the choice of the period are linked and depend on the investigated temperature, as shown on Fig. 3 [16]. This is a result of the heat



**Fig. 3** Evolution of the couple amplitude-period of modulation vs. temperature, showing the maximum values of both amplitude and period at a given temperature

exchanges which depend also on the cooling system used; in the present study a liquid nitrogen cooling system was used to monitor the modulation. Figure 3 shows the upper limiting envelop for the values of the pair period-amplitude that must be used depending on the investigated temperature range.

Finally, the choice depends also on the temperature scanning rate to be used. Effectively, the superimposition of a modulation, with fixed period and amplitude, to a linear ramp yields a 'modulated temperature', introducing then the notion of punctual temperature scanning rate with extremes  $q_{\max}$  and  $q_{\min}$  defined as follows:

$$q_{(\max \text{ or } \min)} = q \pm A_T \frac{2\pi}{p} \quad (4)$$

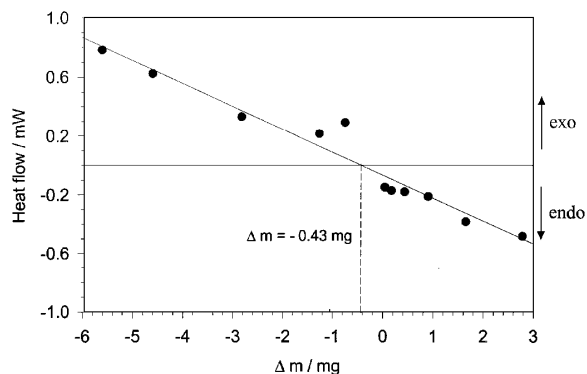
where  $q$  is the average scanning rate.

This particularity allows, contrary to DSC, to use low average scanning rates to increase the resolution of the signal. In this way, separation of multiple peaks is possible without loss of sensitivity, thanks to the advantage of having local high scanning rates.

A particular selection of the experimental parameters can lead to a special mode called 'heat only mode' for which the temperature scanning rate is always positive. In other words, there is no cooling during the modulation, allowing, when necessary, to control the heating in a continuous way without erasing or modifying (by cooling) the 'instantaneous history' of the sample. Moreover, when the average scanning rate  $q$  is equal to zero, the quasi-isothermal mode created allows the determination of the heat capacity of the sample closed to equilibrium conditions.

Following strictly the conditions described above in order to avoid any distortion of the modulated signal, the reproducibility of measurements will depend greatly on the preparation of the sample. Effectively, it is essential to insure a perfect thermal contact between the sample and its pan on one side (it is recommended to use films to obtain something completely flat) and, on the other side, between the pan and the platform on which the DSC cell is resting. For the same reason, thick or massive samples must be avoided; nevertheless, the limits of the methodology in terms of sensitivity and precision are highly depending upon the characteristics of the sample investigated.

To avoid possible errors (in the case of modulated mode) of the order of magnitude of  $\pm 2a_b$  – see Eq. (1) – on the estimation of the baseline, when using Eq. (2), it was necessary to overcompensate the temperature-dependent asymmetry of the cell by increasing the mass of the sample pan [17]. On Fig. 4 are represented the results of the artificial asymmetry created (in the case of the TA DSC 2920) when varying  $\Delta m = m_s - m_r$  during heating runs of  $5 \text{ K min}^{-1}$ ;  $m_s$  and  $m_r$  are the masses of the empty aluminium pans holding respectively the sample  $s$  and the reference  $r$ . At the temperature of the experiment, 315 K, the value of the imbalance (i.e. the value for which the obtained differential heat flow is zero) is of the order of  $-0.43 \text{ mg}$  (Fig. 4). This means that to insure a necessary negative heat flow during the heating, the  $\Delta m$  value must be higher than  $-0.43 \text{ mg}$ . In other words, to be on the safe side, it is recommended to use for all measurements under modulation, in the case of the TA DSC

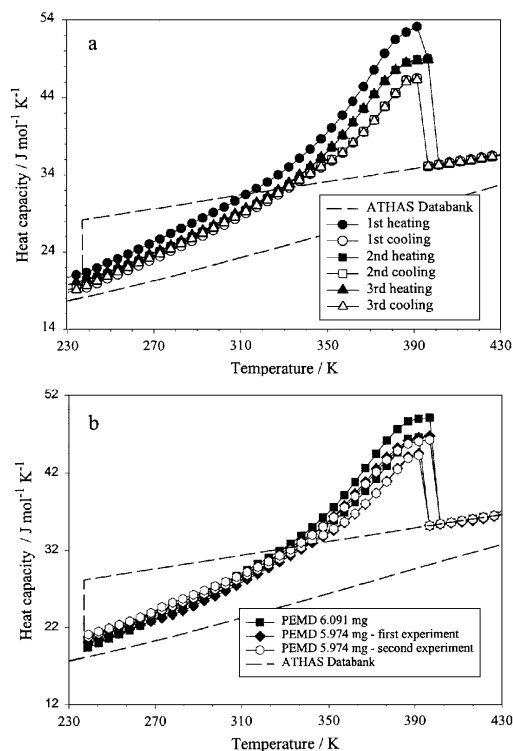


**Fig. 4** Plot of the differential heat flow vs. the difference  $\Delta m$  between the masses of the sample and reference pans in the case of the TA TMDSC 2920. Measurements were made during heating runs realized at  $5 \text{ K min}^{-1}$ ; values have been taken at 315 K. The endothermic and exothermic sides have been indicated

2920, a  $\Delta m$  much larger than  $-0.43 \text{ mg}$ . As a matter of fact, Boller et Wunderlich have shown [17] that the asymmetry is a function of both, mass difference and temperature. At the temperature of 355K for example,  $\Delta m$  has a value of  $-0.51$ . Therefore, a  $\Delta m$  of about 1.5 mg seems to be sufficient to overcome the effect of temperature-dependent asymmetry. This asymmetry is proper to each instrument and has to be determined before any experiment realized under modulation.

#### *Determination of heat capacities using the quasi-isothermal mode*

The heat capacity at constant pressure is a calorimetrically measured quantity. As seen previously, the choice of the experimental parameters like the sample mass and the heating rate for a given run depends largely on the sample. As regards the mass of sample, the value depends on the sensitivity of the calorimeter used and must be selected accordingly; best results were obtained with 3 to 9 mg of MDPE with the TA DSC 2920 and with 20 to 30 mg with the Mettler-Toledo DSC 821 [18]. Usually, the determination of heat capacities by conventional (non-modulated) DSC suffers from a well-known drawback: it crucially depends on the long-term stability of the baseline of the instrument and measurements are not done under quasi-isothermal conditions. In order to circumvent these difficulties, different dynamic methods using non-linear temperature profiles, were developed. For our study with MDPE, the TA DSC 2920 was used in the modulated temperature mode. Figures 5a and b show the results for heat capacities obtained in quasi-isothermal conditions during successive fusions and crystallizations of one sample of 6.091 mg of MDPE (a), and the comparison between two different samples of 6.091 and 5.974 mg respectively (b). For the representation of the results in Figs 5a and b the values in the liquid state have been 'corrected'; that is to say, shifted to be identical to the 'reference' values given by the ATHAS Databank [19]. This, in order to compare all the different runs



**Fig. 5** Quasi-isothermal runs on successive 3 heatings and 3 coolings of one sample of 6.091 mg of MDPE (a). Comparison of the results for the second runs obtained with two samples of MDPE, of 5.974 and 6.091 mg respectively. The points correspond to different runs; full curves are drawn through the points. Dash lines represent the values corresponding to crystallized solid and liquid phases respectively. Measurements were taken with the TA TMDSC 2920 (b)

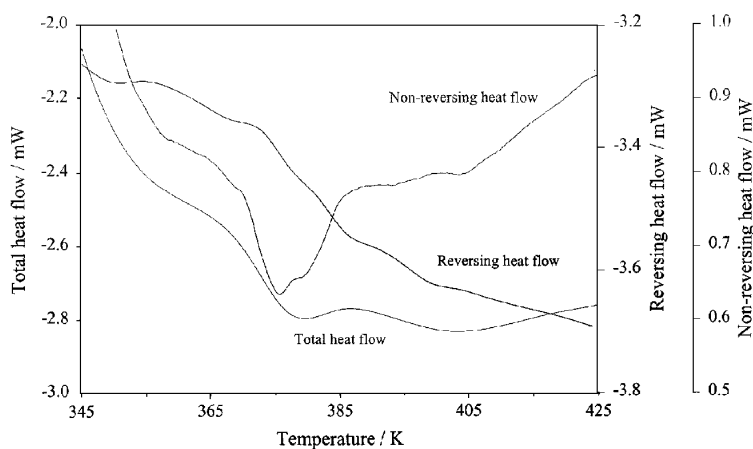
in some normalized way. Each point represents an average value of the last 10 min of a 20 min time-period experiment to be sure that real stability (i.e. equilibrium) has been reached during the measurement. This kind of measurement allows a better determination of the heat capacity curve as a function of temperature, because the results are more reproducible than those obtained with the conventional method. This is certainly true also for fusion and crystallisation due to the possibility to reach a steady state at each temperature. In Fig. 5a, the first heating is distinguishable from the other runs this, because of a different unknown thermal history; the sample was indeed studied 'as received'. For the Fig. 5b, only the second runs of the same kind of experiment realized for Fig. 5a are represented to allow a comparison of samples with the same thermal history. As a consequence of the sequence fusion-crystallization, a small amount of locally reversing melting can be observed, which crystal-



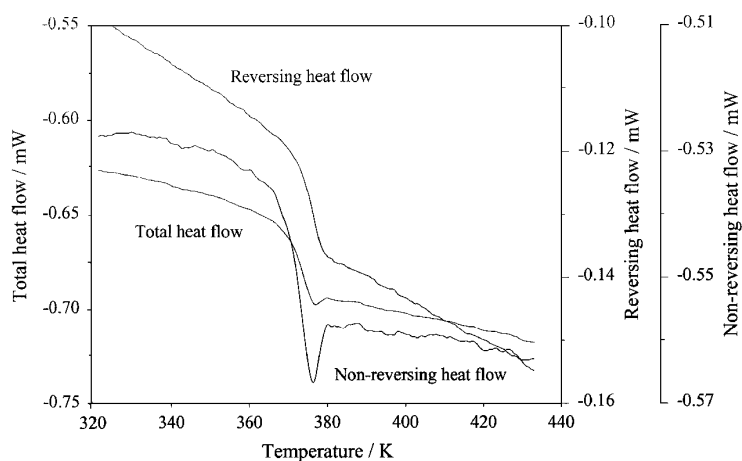
lizes again during every cooling cycle, like it has been observed with (polyethylene terephthalate) PET and (polyethylene oxyde) PEO [20–22].

*Advantages of the separation of the total heat flow into the reversing and the non-reversing heat flows*

One of the major advantages of the technique described in this work is most probably the possibility to access directly in a single run to overlapping effects. In the case of an epoxy resin taken as an example [23] – see Fig. 6 –, the separation of



**Fig. 6** Total, reversing and non-reversing heat flows for an epoxy resin, obtained with the TA TMDSC 2920 with the temperature scanning rate  $q=2 \text{ K min}^{-1}$ , the modulation period  $p=50 \text{ s}$  and the temperature modulation amplitude  $A_{T_s}=0.5 \text{ K}$



**Fig. 7** Separation of the total heat flow, generated during a run with a polystyrene sample, into its two components, reversing and non-reversing. Measurements were taken with the Mettler-Toledo DSC 821

the reversing and non-reversing heat flows allows to distinguish (in the reversing heat flow) the glass transition of the epoxy resin, masked by the evaporation of water in the non-reversing heat flow. Evidently, conventional DSC can be used also to determine the glass transition but, in two consecutive runs; that is to say in a second run, after only evaporation of water has occurred in the first one. However, this procedure does modify the thermal history of the sample since the rate of cooling consequently modifies the characteristics of the sample. In this respect, temperature modulated DSC appears to be a more powerful technique. The second example, to illustrate this capability of the technique, is the separation of the glass transition from the relaxation phenomena that overlap. This separation, showed on Fig. 7 for a PS sample studied with the Mettler DSC 821, enables to not only determine the exact temperature of the glass transition of the sample through the reversing heat flow but, also, to quantitatively evaluate its history, in terms of thermal, mechanical or chemical contributions. This information is 'contained' in the peak (the minimum) exhibited by the non-reversing heat flow; integration of this peak yields the amount of energy quantifying then the non-reversing changes undergone by the sample.

Recent work on PS modified by supercritical methane [1] at different high methane pressures has shown that the polymer glass transition (observed on the reversing heat flow) does remain identical whereas the non-reversing heat flow shows different (non-reversing) relaxation peaks corresponding to the different pressures to which the polymer samples have been submitted [24].

## Conclusions

Thanks to constant improvements in the methodology and better mastering of the parameters involved, modulated temperature thermal analysis techniques, particularly in the quasi-isothermal mode which is possible by some form of modulation of the temperature, allow to obtain more accurate results for a better understanding of the thermal behaviour of polymers. Furthermore, an attractive aspect of these techniques is certainly the possibility to separate the total heat flow, similar to the signal obtained in the case of the conventional DSC, into two components containing different pertinent informations and not directly accessible otherwise.

Good precision and reproducibility of the results necessitate the total control of the different key parameters of the method as well as the strict control of the temperature modulation to keep it without any distortion. When mastering the experimental conditions (average scanning rate, period and amplitude of modulation), temperature modulated DSC is a powerful technique which can also be used for example to study first order transitions; this is typically illustrated by a previous work [25] on the reversibility of the fusion of indium.

## References

- 1 M. Ribeiro, PhD Thesis, Université Blaise Pascal, France, 1998.
- 2 A. F. Barnes, M. J. Hardy and T. J. Lever, *J. Thermal Anal.*, 40 (1993) 499.
- 3 A. Cesàro, L. Navarini and E. Pepi, *Thermochim. Acta*, 277 (1993) 157.

- 4 D. Q. M. Craig and F. A. Johnson, *Thermochim. Acta*, 248 (1995) 97.
- 5 L. N. Bell and D. E. Touma, *J. Food Sci.*, 61 (1996) 808.
- 6 P. F. Sullivan and G. Seidel, *Phys. Rev.*, 173 (1968) 679.
- 7 O. M. Corbino, *Phys. Z.*, 12 (1911) 292.
- 8 T. Hashimoto, J. Morikawa, T. Kurihara and T. Tsuji, *Thermochim. Acta*, 304/305 (1997) 151.
- 9 Y. Saruyama, *Thermochim. Acta*, 304/305 (1997) 171.
- 10 I. Alig, *Thermochim. Acta*, 304/305 (1997) 135.
- 11 M. Reading, D. Elliott and V. L. Hill, *J. Thermal Anal.*, 40 (1993) 949.
- 12 J. E. K. Schawe, *Thermochim. Acta*, 261 (1995) 183.
- 13 D. G. Archer, *J. Phys. Chem. Ref. Data*, 22 (1993) 1441.
- 14 Advanced Thermal Analysis (ATHAS). University of Tennessee 8<sup>th</sup> Report (1995). See also B. Wunderlich, Y. Jin and A. Boller, *Thermochim. Acta*, 238 (1994) 277.
- 15 M. Varma-Nair and B. Wunderlich, *J. Thermal Anal.*, 46 (1996) 879.
- 16 TA Instruments, Report 1994. See also A. Boller, Y. Jin and B. Wunderlich, *J. Thermal Anal.*, 42 (1994) 307.
- 17 A. Boller, I. Okasaki, K. Ishikiriyama, G. Zang and B. Wunderlich, *Thermochim. Acta*, 49 (1996) 1081.
- 18 M. Ribeiro, A. Boller, L. Rodier, J.-P. E. Grolier and B. Wunderlich, *Calor. et Anal. Therm.*, 28 (1997) 2.
- 19 U. Gaur and B. Wunderlich, *J. Phys. Chem. Ref. Data*, 10 (1981) 119.
- 20 I. Okasaki and B. Wunderlich, *Macromolecules*, 30 (1997) 1758.
- 21 I. Okasaki and B. Wunderlich, *Macromol. Chem., Rapid Commun.*, 30 (1996) 313.
- 22 K. Ishikiriyama and B. Wunderlich, *Macromolecules*, 30 (1997) 4126.
- 23 Commercial product. Confidential Report from our laboratory.
- 24 M. Ribeiro, S. L. Randzio and J.-P. E. Grolier, to be published.
- 25 A. Boller, M. Ribeiro and B. Wunderlich, *J. Therm. Anal. Cal.*, 54 (1998) 545.