

# Heat Capacity Measurement in Polymers Using a Differential Scanning Calorimeter: Area Measurement Method

F. Hernández-Sánchez

Centro de Investigación Científica de Yucatán, A. C., Calle 43 No. 130, Col. Chuburná de Hidalgo, 97200, Mérida, Yucatán, México

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**ABSTRACT:** It has always been difficult to determine the heat capacity of a polymer experimentally. However, with the arrival of differential scanning calorimetry, the determination of such heat capacity could be achieved more quickly, but the precision of the measurement was always limited by the need to correlate the relative heights of thermogram signals obtained from the polymer under study and a standard reference material. The technique reported in this article is as fast as the traditional tech-

nique in differential scanning calorimeter, but the accuracy of the measured heat capacity is high because it is based on the measurement of areas rather than determination of height differences. In addition, it is not necessary to use a standard sample as a reference. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3562–3567, 2007

**Key words:** heat capacity; differential scanning calorimetry; DSC; thermal absorptivity; thermal inertia

## INTRODUCTION

In differential scanning calorimetry, the heat flow in a sample is measured during a temperature change; it maintains the heating or cooling of the sample and registers the release or absorption of heat due to a phase transition. Therefore this technique is particularly useful for the measurement of changes in thermal properties, such as heat capacity change during a glass transition, the determination of heats of fusion or crystallization of a semicrystalline polymer, a chemical reaction kinetics, etc. Absolute heat capacity at a constant pressure ( $C_p$ ) can be also measured, but a standard sample with known  $C_p$  is needed.  $C_p$  is determined by comparison of the signals from the material and the standard sample.<sup>1,2</sup>

Upon initiating an experiment in a differential scanning calorimeter (DSC) by setting a heating or cooling scan rate, the first signal readings that appear are usually associated with the stabilization of the system, that is, a "transient state." After the system overcomes this initial transient state, a continuous steady regime of constant heating or cooling is achieved, and this is reflected in a stable baseline that will change only in the events that are derived from thermal transitions in the sample.

This transient state is known as thermal absorptivity\* and is defined as:<sup>2</sup>

$$I \equiv \sqrt{k\rho C}$$

where  $k$  is bulk thermal conductivity,  $\rho$  is bulk density, and  $C$  is the heat capacity. This equation represents the material's ability to conduct and store heat, which can be seen as the material's resistance to temperature change.<sup>3,4</sup> In DSC thermograms with a scan rate, the initial signal corresponds to the heat absorptivity by the ovens and of the sample. This signal corresponds to a change of state from an isothermal state to a scan rate state.

The heat capacity is the amount of heat necessary to elevate the temperature of a mass by 1 K, in this case, at constant pressure ( $C_p$ ). Therefore, if the DSC is capable of changing the oven temperature (by 1 K) quickly enough in relation to the sample, then it should be possible to isolate the signal corresponding to the sample. If this is achieved, then the  $C_p$  can be measured.

This work focuses on the study of this transient signal, which can be related to the heat capacity of the material. Then, the behavior of a polymer mass as a function of the different heating rates upon increase of the temperature by 1 K is analyzed. This characterization provides experimental evidence of

Correspondence to: F. Hernández-Sánchez (fhs@cicy.mx).

\*In other areas of science, such as astronomy<sup>3</sup> and physiology<sup>4</sup>, eq. (1) is known as thermal inertia.

**TABLE I**  
**Characteristics of the Polymers Used**

Sample	Provided by	Molecular weight	Polydispersity
Isotactic polypropylene (iPP)	American Polymer Standard Corp.	108,000	3.32
Polyethylene (PE), density (g/cc): 0.94	Scientific Polymer Products	108,000	1.32
Polystyrene (PS)	Polysciences, Inc.	200,000	1.06
Aluminum oxide (sapphire)	Perkin-Elmer	101.96	

the possibility of measuring the heat capacity without the need for the lengthy and involved procedure of comparing signals between the sample and a standard, as it is done in the classical method used by different differential scanning calorimeters commonly used.

### MATERIALS AND METHODS

The polymers used and their characteristics are shown in Table I.

A DSC Perkin-Elmer model 7 and a DSC Perkin-Elmer model Pyris 1 were used. Both DSCs were cooled using an intracooler, which remained switched on throughout the experiment. Before starting the experiment, the intracooler was left on for 6 h to stabilize the temperature chamber. The DSC-7 was connected to a 1022TA Perkin-Elmer data station with DT software.

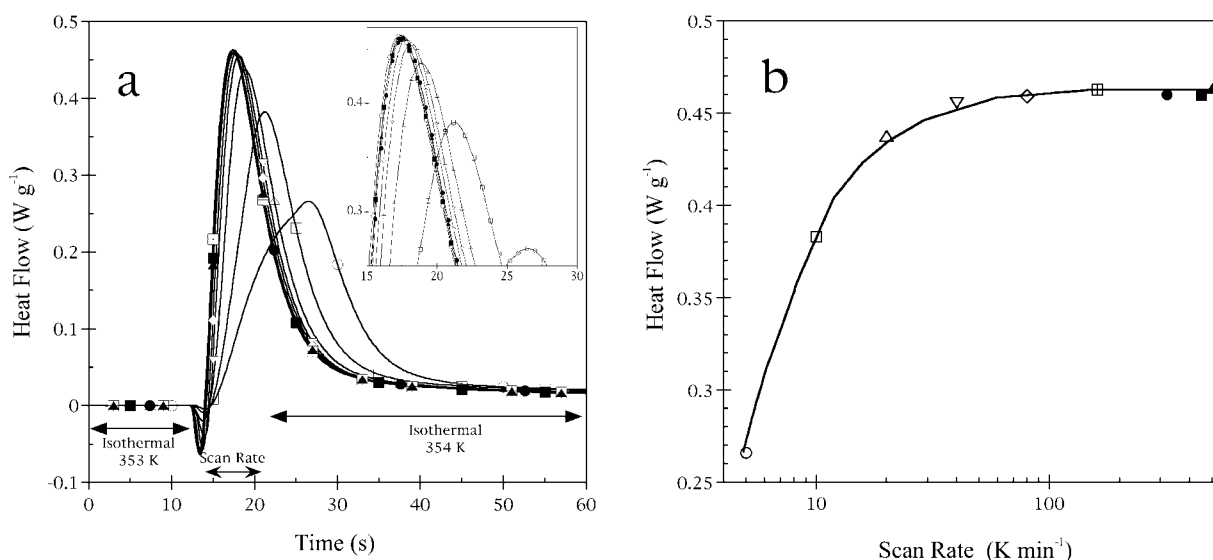
Pans for solids were used with polymer in powder form. The sample was prepared by first heating up to the melting point, and then the cover pan was pressed to shape the polymer to the mold to obtain the largest possible polymer surface area in contact with the pan walls. The sample mass was between 15 and 18 mg. An empty pan was used as a reference.

An isothermal scan was programmed to go from  $T$  to  $T + 1$  in 0.1335 s, which is equivalent to a scan rate of 450 K/min.  $T + 1$  was maintained for 5 min. An isothermal scan was used in the DSC-7, and in the case of the Pyris 1, a step-scan isothermal mode in the DSC, both starting at  $T$  and a scanning of 450 K/min to reach  $T + 1$ , and then maintaining this temperature for 5 min.

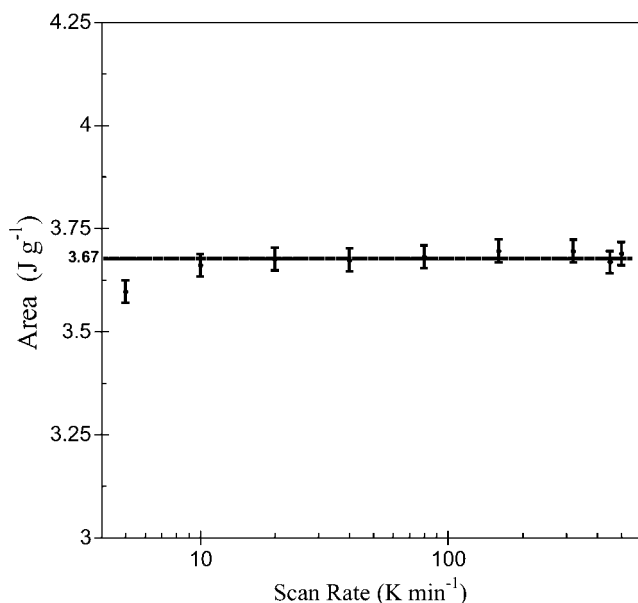
It should be remembered that when using a DCS, the calibration of the temperature and of the heat is very important. In this case, the DSC was calibrated using the heat of fusion of tin and the fusion temperatures of tin and lead. This calibration is important to collect  $C_p$  quantitative data with good precision for this study.

### RESULTS AND DISCUSSION

As shown in Figure 1(a), to reach the temperature increment more quickly, it is necessary to increase the heat flow. In the figure, each curve corresponds to a different heat flow for each scan rate. It should be noticed that the higher the heating rate a higher signal peak is obtained. Also, it should be noticed that for high heat flow there is no increase in the endothermic peak [Fig. 1(a) insert]. Figure 1(b) shows the behavior



**Figure 1** (a) Isothermal thermograms for the iPP at different scan rates for the start 353 K at end 354 K temperatures (DSC-7). (b) Maximum heat flow for different scan rates. Scan rate (K/min): 5, ○; 10, □; 20, △; 40, ▽; 80, ◇; 160, ▢; 320, ●; 450, ■; 500, ▲.



**Figure 2** Area calculation for different scan rates.

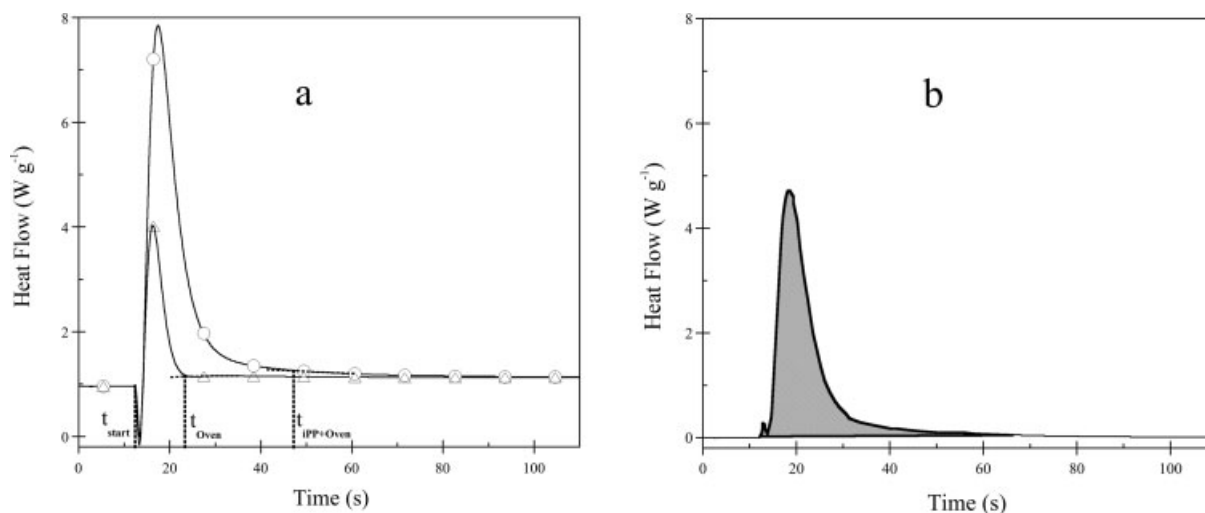
of the maximum heat flow values in the experiment. As can be seen, the behavior becomes asymptotic at 0.46 W/g for ramps over 80 K/min. This means that the heat flow is the same. It is believed that for heating rates lower than 80 K/min, the material properties  $C_p$  and  $k$  govern the heat transfer to the sample, whereas for higher heating rates such a transfer mechanism is governed by temperature in the oven; in other words, the sample will take the heat it requires to increase its temperature by 1 K from the oven. The area below the thermogram curve in Figure 1(a) represents the heat required by the system (oven + PS) to increase the temperature of the sample by 1 K.

Figure 2 shows the value of the areas below each curve as a function of the scan rate. As can be seen,

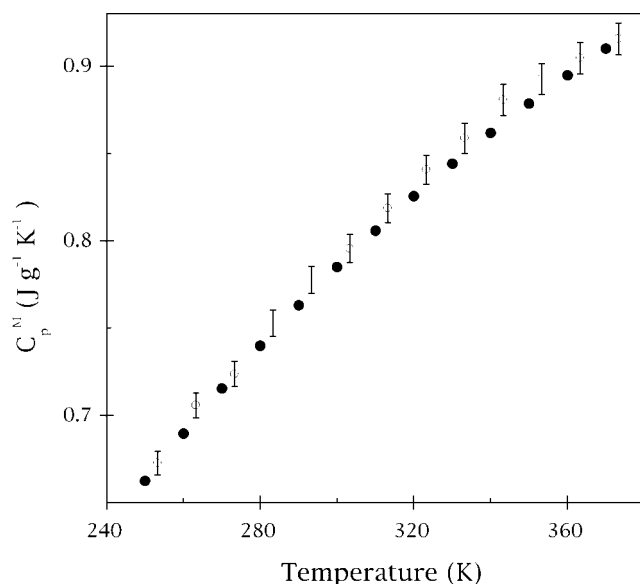
the area is the same independent of the scan rate used. Taking into account the fact that the experimental error for the values in the area, it can be seen that only the scan rate for 5 K/min is outside the horizontal line shown by the other experimental points. This may be because of the fact that the signal from a DSC depends on the scan rate and mass (among other things), and so a higher experimental error will be obtained with small endothermal peak (<5 K/min).

Using the thermogram corresponding to a scan rate of 450 K/min, shown in Figure 1, the heat capacity for a polymer can be determined as follows:

1. The DSC is programmed so that the oven goes from temperature  $T_0$  to temperature  $T_0 + 1$ , with a scan rate of 450 K/min.
2. An experiment is carried out with empty DSC pans. The thermogram obtained corresponds to the entire system, including the DSC electronic impedance and the thermal inertia of the DSC ovens. This signal has the lowest endothermal peak, shown in Figure 3(a).
3. Another experiment is carried out under the same conditions as in paragraph 2, but this time with the polymer sample. This signal corresponds to the highest peak shown in Figure 3(a). In addition to containing the information of the polymer, it also contains the information corresponding to the DSC electronics impedance and the thermal inertia of the DSC ovens.
4. The thermograms shown in Figure 3(a) represent the heat flow per mass unit at each time for the experiments described in paragraphs 2 and 3, and therefore, it is possible to subtract the two endothermal peaks point by point to



**Figure 3** (a) Oven,  $\circ$  and ovens + iPP,  $\triangle$  system thermograms. (b) Subtraction oven + iPP system and oven thermograms (DSC-7).



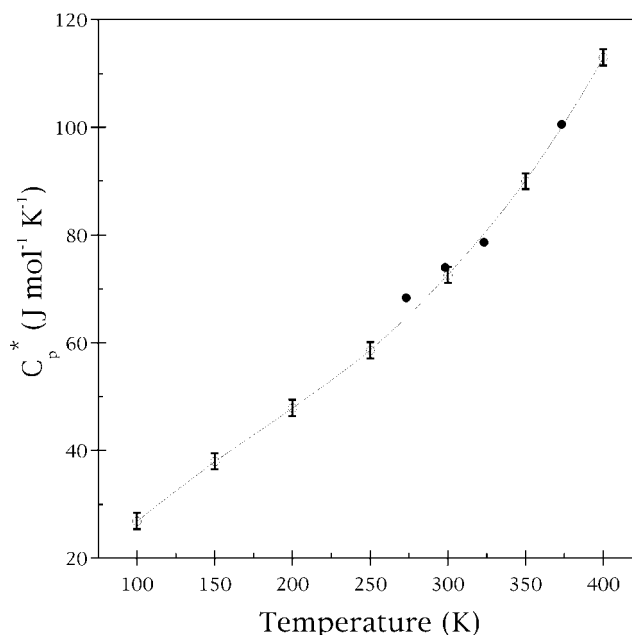
**Figure 4** Sapphire mass heat capacity compared with data from the literature: data experimental,  $\circ$  and Manual DSC-7,  $\bullet$ . Performed with DSC-Pyris 1.

obtain only the endothermal peak for the polymer, Figure 3(b).

- Figure 3(b) represents the heat flow per mass unit for the polymer because of a temperature increase by 1 K. Consequently, the area under the curve of this endothermal peak represents the heat by mass unit required by the sample to increase its temperature by 1 K, that is, the  $C_p$  (areas measurement method; AMM).

Subtraction of the two thermograms in Figure 3(a) must give an endothermal peak sufficiently large to ensure that the error in the area calculation is small, and therefore, the  $C_p$  determination will be highly accurate. This will be possible if the time the DSC oven takes to change its temperature by 1 K is less than one-third the time it takes for the oven + iPP to change its temperature, that is  $(t_{\text{oven}} - t_{\text{st}})/(t_{\text{iPP+oven}} - t_{\text{st}}) < 1/3$  [Fig. 3(a)], where  $t_{\text{st}}$  is the initial time of the experiment, for both the oven alone and the oven containing the iPP sample and  $t_{\text{oven}}$  is the final time for the experiment with only the oven and  $t_{\text{iPP+oven}}$  is the final time for experiment with oven plus iPP.

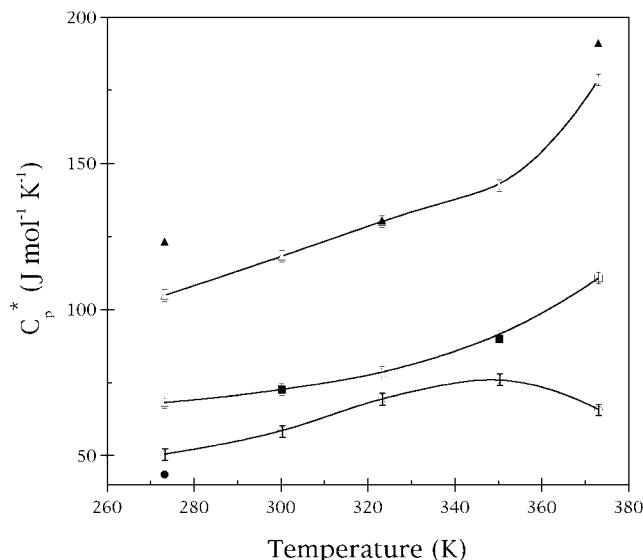
Figure 4 shows the experimental mass  $C_p^M$  measured for sapphire typically used as a reference material for  $C_p$  measurements and a comparison with the values reported in the literature.<sup>5</sup> As can be seen, there is a good agreement between the measured and the reported values for this material. Hence, the use of sapphire as a standard could be omitted, since the AMM reproduces literature values. With the proposed AMM, a reference material (for the measurement of  $C_p$ 's) is not necessary, as for



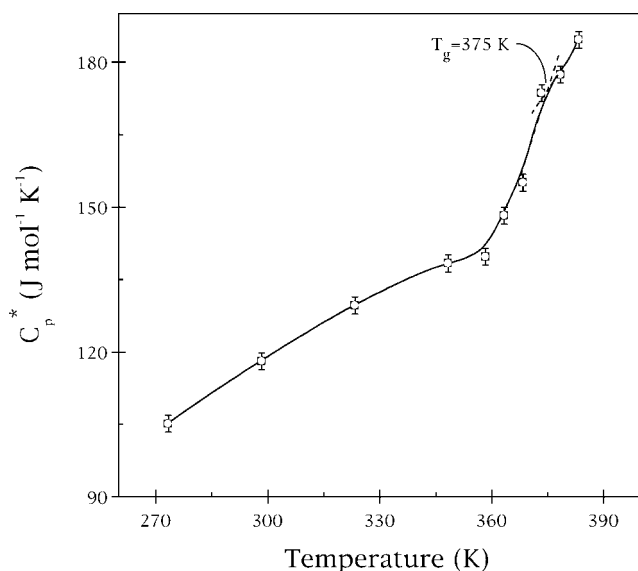
**Figure 5** Molar heat capacity for iPP, experimental data,  $\circ$ ; Polymer Handbook data for iPP,  $\bullet$ . Performed with DSC-7.

the standard calibration procedures of the DSC. Nor it is necessary to perform several experiments to obtain an average of the heat flow, since the areas under the curves are measured and they represent the heat capacity of the material. Thus, the measurements are independent from the origin, as in the case of heat fusion calculations.

To assess the reproducibility of the proposed method, the  $C_p$ 's for three reference polymer samples



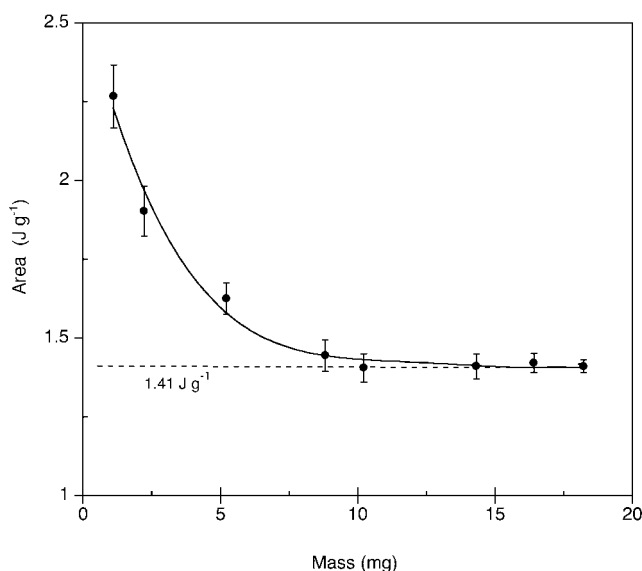
**Figure 6** Molar heat capacity for PE: experimental data,  $\circ$ ; Hand Book data,  $\square$ ; for iPP: experimental data,  $\bullet$ ; Hand Book data,  $\blacksquare$  for PS: experimental data,  $\blacktriangle$ ; Hand Book data,  $\blacktriangle$ . Performed with (DSC-7).



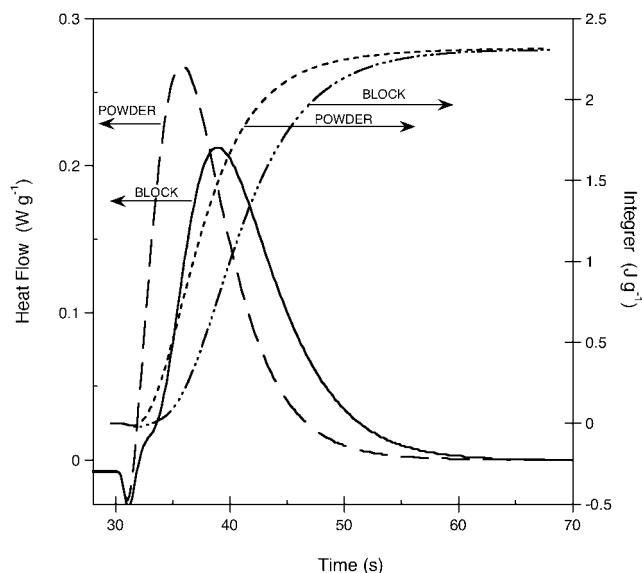
**Figure 7** Molar heat capacity as a function of temperature, typical plot for amorphous PS. Performed with (DSC-7).

(Table I) were determined. Five experiments for each of polymer were performed. Excellent agreement between all the results and the value of the area below the peak showed a difference of  $\sim \pm 1.5\%$ . This means that a single sweep is sufficient to obtain a good  $C_p$  value.

Figure 5 shows the values of the experimental molar  $C_p^*$  for iPP, for four different temperatures values at a scan rate of 450 K/min. The  $C_p^*$  values of iPP obtained from the literature are also shown.<sup>6</sup> As can be observed, all the points, both experimental and those obtained from the literature, agree well on a curve.



**Figure 8** Area as a function of sample mass.



**Figure 9** Comparison of areas between samples of the same polymer, one in solid block form and the other in powder form.

Results obtained for iPP, PE and PS are shown in Figure 6. In all three cases, the experimental points agree well with those obtained from the literature.<sup>7</sup> In the case of PE, for temperatures higher than 360 K, the  $C_p^*$  decreases; this represents an apparent contradiction, since the  $C_p^*$  of a material increases when the temperature increases. This may be because of the fact that the signal consists of at least two contributions: the heat absorption by specific heat and a small amount of latent heat, being both endothermal contributions. We must recall that the melting point of low density PE is  $\sim 388$  and 408 K for high density PE. The melting endotherm for PE shows a broad process; however, it is also, very likely, that the PE recrystallization heat starts to show up in this area (exothermal contribution). In this latter contribution, the endotherm area is reduced in size because the sample may be generating a small amount of heat.

Figure 7 shows a plot of  $C_p^*$  versus temperature for PS, for a temperature range where the glass transition takes place. The shape of this curve is typical of those found for the glass transition in amorphous polymers.<sup>7</sup>

#### Additional comments

Figure 8 shows the behavior of the area by mass unit as a function of mass. As can be seen, this behavior is asymptotic up to a value of 1.20 J/g for a 15 mg mass. This means that for masses smaller than 15 mg, the thermal absorptivity of the polymer is comparable with the thermal absorptivity of the oven. Therefore, the heat varies as a function of mass of the sample. It is therefore important to use at least 15 mg of polymer.

Figure 9 shows the thermograms (heat flow versus time) obtained from a single sample of PS, with the difference that one is in a solid block form and the other is a powder form. It can be seen that the peaks are quite different, but the total area is the same. This means that the kinetics (given by the shape of the curve of the heat flow integral) to increase the sample temperature 1 K is different. The powder requires a greater heat flow but less time to complete the process. This is because of the effects of heat diffusion that are different one from other, because the bulk thermal conductivity is different for both, solid block and powder form polymer.

### CONCLUSIONS

This method is based on the initial signal of thermograms, which is normally disregarded as it corresponds to a transitory state, with the sample going from an isothermal state to a dynamic state with a prescribed temperature rise rate. Measuring areas is a quick method for obtaining the heat capacity using any standard DSC with low thermal absorptivity oven. Unlike the traditional technique, the proposed method is more accurate as it measures areas rather than heights. The precision of the  $C_p$  measurement proposed here depends on how accurately the DSC is calibrated with commercially available reference

materials such as indium, tin, lead, etc., which are generally used depending on the temperature range in which the experiments are carried out. This calibration is important for obtain good results.

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