

# Simultaneous Gravimetric and Calorimetric Analysis of Chloroform Sorption in Nanoporous Semicrystalline sPS

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**ABSTRACT:** Chloroform vapor sorption in semicrystalline syndiotactic polystyrene with a nanoporous crystalline form has been investigated by simultaneous gravimetric and calorimetric analysis to gather information on the sorption process and associated heat of sorption. At the investigated pressures of chloroform vapor, the sorption process is dominated by exothermic adsorption of penetrating molecules in the nanocavities of the crystalline phase. The mass uptake kinetics has been compared with the kinetics of evolution of

heat of sorption measured simultaneously. The integral heat of sorption evaluated calorimetrically has been compared to the corresponding value calculated by elaborating gravimetric sorption isotherms at several temperatures evaluated independently through gravimetric sorption experiments.

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## INTRODUCTION

Sorption and diffusion processes of low molecular weight compounds in polymers have a great importance in many industrial applications, such as packaging and separation membranes, controlled drug delivery, and environmental resistance of polymer matrices.

In general, a polymer displays both a crystalline and an amorphous domain, in which sorption and diffusion mechanisms are different. It is widely accepted, in fact, that sorption takes place only in the amorphous region, where macromolecular network organization and mobility offer enough space for the molecular diffusion and sorption.<sup>1</sup> Instead, the compact crystalline domain makes the diffusion of the penetrating molecules through the bulk structure more difficult, and their solubility in the crystalline domain is almost zero. Few notable exceptions have been reported in the literature, as is the case of semicrystalline poly(4-methyl-1-pentene),<sup>2,3</sup> which is characterized by a limited but not negligible solubility of low molecular weight penetrants in the crystalline phase.

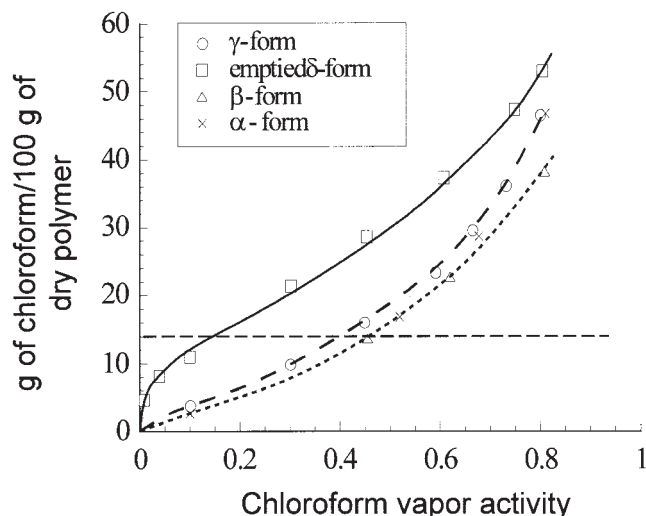
Syndiotactic polystyrene (sPS) is a low cost semicrystalline polymer that displays a complex polymorphic behavior.<sup>4–7</sup> The various crystalline modifica-

tions differ with respect to the chain conformation, as well as for the chain packing within the unit cell. Referring to the nomenclature proposed in the literature,<sup>6</sup> four main crystalline forms may be distinguished, denoted, respectively,  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ . The first two,  $\alpha$ <sup>8–10</sup> and  $\beta$ ,<sup>4,11</sup> have the chains in a *trans*-planar, zigzag conformation with identity period 5.1 Å, while the  $\gamma$  and  $\delta$ <sup>12</sup> show a helical  $s(2/1)2$  conformation of the chain with identity period of 7.7 Å. Clathrate structures that include several different guest molecules have also been described,<sup>13–15</sup> and it has been recently found that, by using suitable extraction procedures,<sup>16</sup> guest molecules can be removed from the clathrate forms to obtain a nanoporous  $\delta$  form, whose crystalline structure has been recently described.<sup>12</sup>

Several studies<sup>17–19</sup> have shown that this nanoporous crystalline phase, which is less dense than the amorphous phase, is able to absorb several volatile organic compounds, readily forming clathrates in significant amounts, displaying a sorption capacity that is competitive with that observed for activated carbon or hypercrosslinked polystyrene.<sup>12,16,20,21</sup> This behavior is rather peculiar since, to our knowledge, there are no crystalline phases with comparable equilibrium sorbed amounts of low molecular weight compounds.

Sorption isotherms of chloroform at 35°C<sup>20</sup> in samples of semicrystalline sPS characterized by different crystalline forms are reported in Figure 1; relevant qualitative and quantitative differences are evident. In fact, the semicrystalline  $\delta$  form displays a much higher

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**Figure 1** Sorption isotherms of chloroform at 35°C in samples of semicrystalline sPS characterized by different crystalline forms.

sorption capacity at low chloroform activities, where a downward concavity is also evident. In this case, two sorption phenomena are involved: adsorption in crystalline nanocavities (which prevails at low activities) and sorption in the amorphous phase (which becomes significant at high activities).

The thermoplastic nature of sPS, and hence the easy processing and recycling, makes this system very attractive from a technological point of view; moreover, the high sorption capacity of the nanoporous crystalline phase makes this system very relevant from a scientific point of view. The aim of this work is the simultaneous monitoring of the gravimetric and enthalpic effects associated with the absorption process of chloroform molecules in the nanoporous  $\delta$  form of sPS, to gather information on both equilibrium (sorption) and kinetic (diffusion) mechanisms.

## EXPERIMENTAL

### Materials

sPS was supplied by Prof. G. Guerra of the University of Salerno, Dept. of Chemistry. The polymer was synthesized according to the method described in refs. 22 and 23. The polymer fraction insoluble in methyl ethyl ketone is 92%; and the intrinsic viscosity of this fraction, determined in tetrahydronaphthalene at 135°C with an Ubbelohde viscometer, is 0.60 dL g<sup>-1</sup>.

Slabs of semicrystalline sPS with nanoporous  $\delta$  form were obtained by casting from chloroform solution at room temperature followed by 5 h extraction with boiling acetone, and by desiccation under vacuum at 60°C for 1 h. The sheets of polymer were then ground to obtain a powder with an average dimension of 10  $\mu$ m.

The crystallinity level is 51% as measured by wide angle X-ray diffraction obtained with nickel filtered CuK $\alpha$  radiation with an automatic Philips powder diffractometer.

### DSC/TG apparatus

Thermogravimetric and calorimetric analysis have been carried out by means of a simultaneous analyzer (differential scanning calorimeter/thermogravimetric analyzer) STA-409 Netzsch, properly modified for this specific work. The apparatus (see Fig. 2) allows the simultaneous measurement of the sample weight variation and of the heat released during the sorption process after a proper calibration procedure.

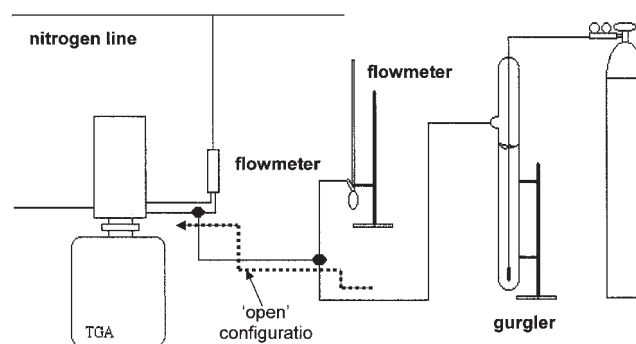
In particular, an apparatus providing a constant flux of nitrogen saturated with chloroform at 20°C has been connected to the STA oven. The flow rate of 120 cc/min in the STA oven can be switched from dry N<sub>2</sub> to chloroform saturated N<sub>2</sub> when thermal equilibrium is reached.

Chloroform vapor activity can be further adjusted by mixing the flows of saturated N<sub>2</sub> and dry nitrogen. Measurements have been performed in isothermal conditions.

The conversion of the measured  $\mu$ V signal to heat flow units (mW) is performed dividing the theoretical value, measured in Ws/g, by the area of the melting peak of a powdered sample of PEG4600 (Aldrich) (melting between 55 and 65°C) measured in units of  $\mu$ V s/g. This comparison led to a calibration ratio, *S*, expressed in mW/  $\mu$ V. The calibration has been repeated using different activity of chloroform at 120 cc/min N<sub>2</sub> flow rate without observing any significant difference. A value of *S* = 1.02 mW/  $\mu$ V was obtained and assumed for the transformation of the raw data in heat flow units.

### The testing procedures

The sPS- $\delta$  powder and the reference (alumina powder) were placed in a standard DSC aluminum pan in the



**Figure 2** Lay-out of the measuring apparatus consisting of a simultaneous analyzer (differential scanning calorimeter/thermogravimetric analyzer) and a system able to provide a constant flux of nitrogen saturated with chloroform.

STA-409 oven. Sample weight for all the tests was in the range of  $9 \pm 1$  mg. The test procedure was:

1. A constant flow of 120 cc/min of dry nitrogen is fluxed in the oven.
2. The oven is heated from ambient temperature to test temperature at 5°C/min.
3. Sample and reference are kept 1 h at the test temperature to reach the thermal equilibrium.
4. A chloroform saturated N<sub>2</sub> flux, mixed with the dry N<sub>2</sub> flux, is fluxed into the STA oven.

Either dry or saturated nitrogen flux of 120 cc/min is always used.

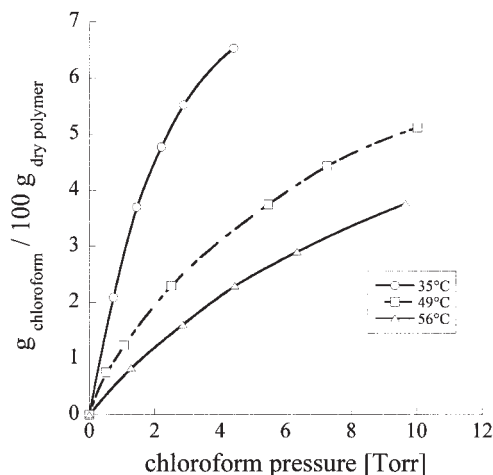
It is worthy of note that it is not possible to establish instantaneously the desired boundary conditions in terms of chloroform concentration in the nitrogen stream since there is a delay due to the dynamics of mixing inside the cell. This delay depends upon the volume of the measuring cell, the pure nitrogen and saturated nitrogen fluxes, and the cell shape.

#### Electronic microbalance with controlled environment

Chloroform vapor sorption isotherms at several temperatures were also determined at 35, 49, and 56°C by hanging the powdered sample, placed in a glass pan, to an electronic microbalance (CAHN D200, sensitivity 0.1 μg) operating at accurately controlled temperature and chloroform pressure. Different from the other apparatus, no nitrogen flow was used and the sample was exposed to pure chloroform vapor. The pan was placed in a water-jacketed chamber with service lines to a reservoir of degassed liquid chloroform, to an accurate pressure transducer (M.K.S. Baratron 121 A, with a full scale of 100 Torr and a sensitivity of 0.01 Torr), and to a turbomolecular pump. Before each sorption run, samples were desiccated under vacuum. Chloroform vapor was then admitted in the cell at the selected pressure. Weight increase due to chloroform sorption was monitored by computer until a constant equilibrium weight was reached. Equilibrium sorption values were then reported versus chloroform vapor activity as gram of chloroform absorbed per gram of dry polymer. The chloroform vapor activity at which each sorption run was performed has been evaluated as the ratio  $p/p_0$ , where  $p$  is the pressure of chloroform vapor at which was performed the sorption run while  $p_0$  is the chloroform vapor pressure at the test temperature.

## RESULTS AND DISCUSSION

Sorption of chloroform at low activities in the semicrystalline sPS empty  $\delta$ -form is expected to occur mainly in the nanocavities of the crystalline phase.<sup>24</sup> In



**Figure 3** Gravimetric sorption isotherms of chloroform at very low activities as measured by gravimetric apparatus at 35, 49, and 56°C.

Figure 3 are reported the gravimetric sorption isotherms of chloroform at very low activities as measured by CAHN apparatus at 35, 49, and 56°C. The downward concavity is related to the progressive approach to saturation of sorption capacity of the crystalline domains. In fact, sorption of low molecular weight compounds in the crystalline domain follows a Langmuir type behavior.<sup>25</sup> As the activity is raised, the contribution of the amorphous fraction of the material increases progressively, as witnessed by the upturn occurring at high activities (see Fig. 1).

The experimental analysis performed by combined heat flow and TGA measurements, to be discussed in the following, has been carried out in an activity range where the adsorption in crystalline nanocavities is the largely prevailing phenomenon.

A significant parameter characterizing the interaction between the polymer matrix and the penetrant is the isosteric heat of sorption ( $q_{st}$ ), which is defined as

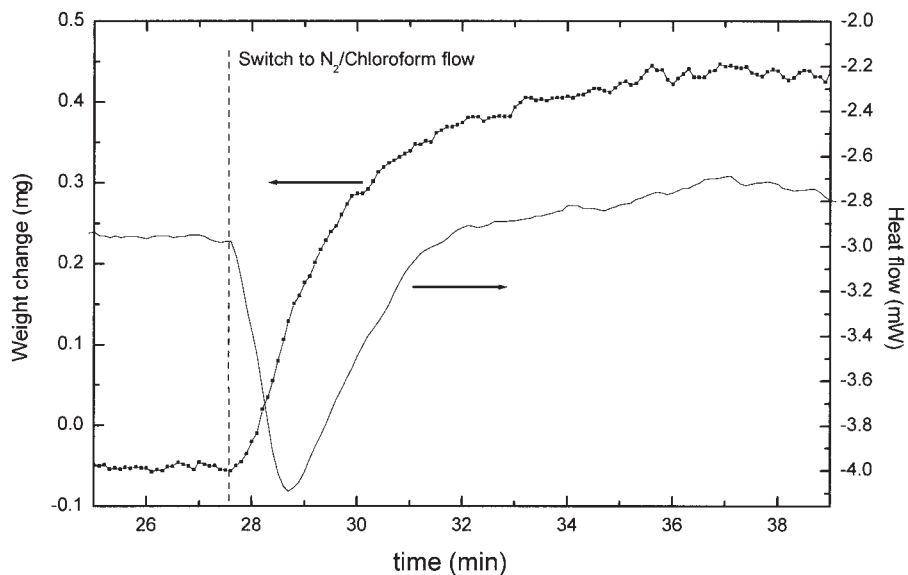
$$q_{st} = (h_2^g - \bar{H}_2^s)_{n_1/n_2} \quad (1)$$

where  $h_2$  and  $\bar{H}_2^s$  represent, respectively, the partial molar enthalpy of the penetrant in the vapor phase and in the polymeric solution.

Using the Gibbs–Duhem equation and making the assumption that both polymer volume change on mixing and partial molar volume of penetrant in the mixture are negligible,  $q_{st}$  can be evaluated operatively as:

$$q_{st} = R \left( \frac{\partial \ln(p)}{\partial (1/T)} \right)_{n_1/n_2} \quad (2)$$

where  $p$  is the chloroform partial pressure in the vapor phase, while  $n_1$  and  $n_2$  represent the number of moles of polymer repeating units and the number of moles of



**Figure 4** Results of the simultaneous calorimetric and gravimetric analysis performed at 35°C on a sample of sPS- $\delta$  exposed to a chloroform activity equal to 0.022.

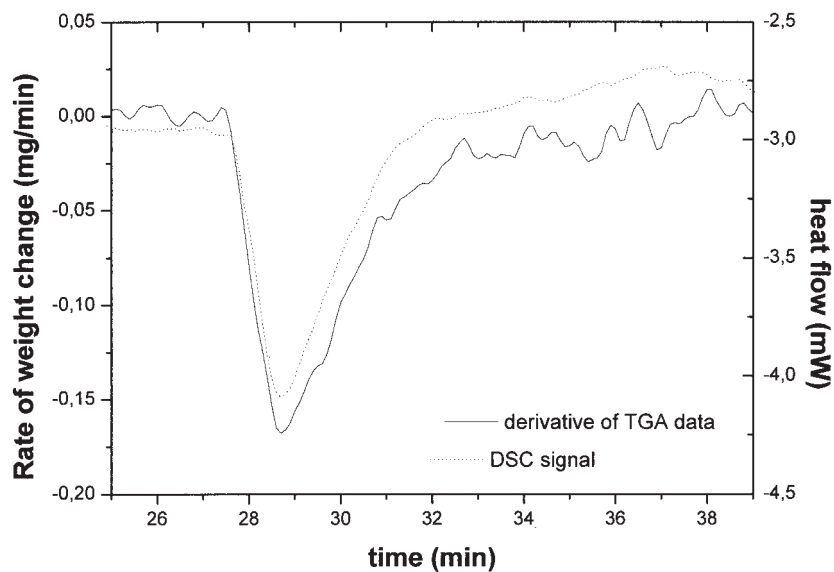
sorbed penetrant. Chloroform sorption isotherms at 35, 49, and 56°C have been analyzed using eq. (2) obtaining an isosteric heat of sorption, which is roughly constant with chloroform concentration and equal to  $500 \pm 20$  J/g. This result will be compared to the findings of calorimetric analysis.

In Figure 4 we report the results of the simultaneous calorimetric and gravimetric analysis performed at 35°C, on a sample of sPS- $\delta$  exposed to a chloroform activity equal to 0.022.

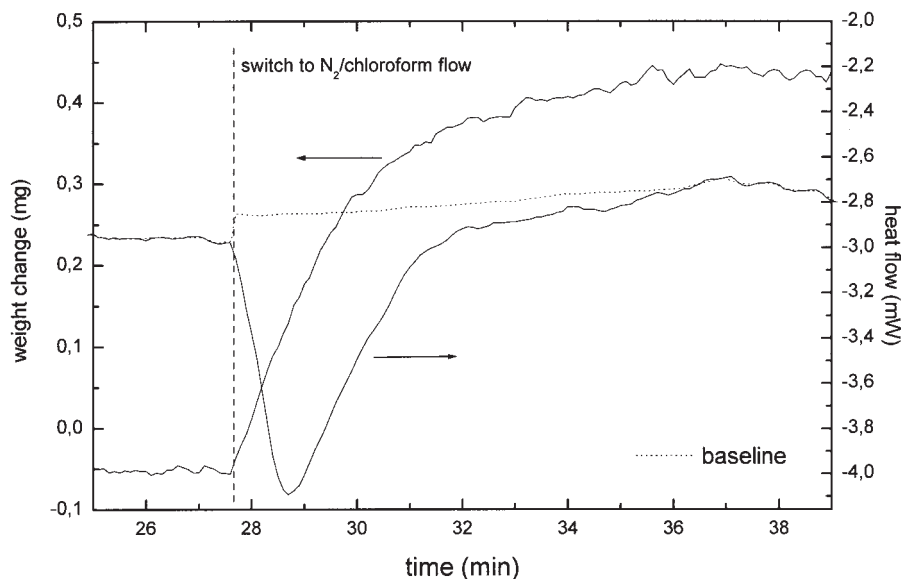
Changes of sample weight due to the sorption process and the associated heat flow are collected as a function of time. The gravimetric signal displays a

sigmoidal shape while the calorimetric plot shows a noninstantaneous response characterized by the presence of a minimum at  $t > 0$ . These features have been attributed to the noninstantaneous establishment of boundary conditions of chloroform activity. As expected, the derivative of mass uptake versus time displays a maximum at the same sorption time as for the heat flux curve (see Fig. 5).

Before contacting chloroform vapor, the sample is in a sorption equilibrium with the pure nitrogen stream. As soon as the chloroform is admitted in the measuring cell, chloroform molecules start to be adsorbed in the nanocavities of sPS, displacing the nitrogen mole-



**Figure 5** Derivative of mass uptake versus time for the sample of sPS- $\delta$  exposed to chloroform.



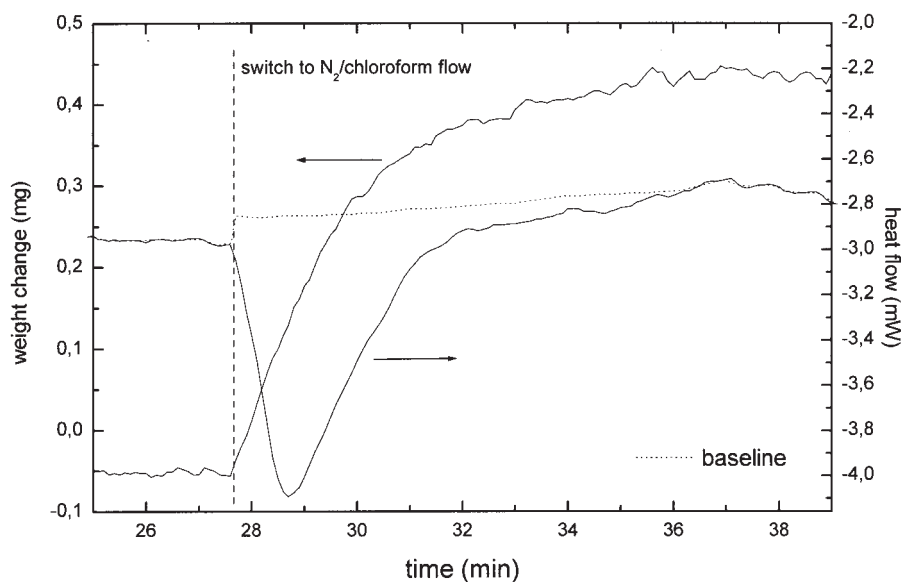
**Figure 6** Illustration of baseline evaluated taking as reference the constant heat flow reached before chloroform exposure.

cules. As a consequence, the calorimetric response involves both the chloroform sorption process and nitrogen desorption.

To evaluate the possible interference from nitrogen desorption, gravimetric sorption tests of nitrogen in the sPS samples have been performed at 35°C at pressures up to 1 atm. A solubility equal to  $0.35 \text{ cm}^3(\text{STP})/\text{cm}^3_{\text{polymer}}$  has been detected at 35°C,<sup>25</sup> which is negligible compared to chloroform solubility. Also, the enthalpy associated to nitrogen desorption, and evaluated by performing sorption experiments at several temperatures, has been found to be negligible (a

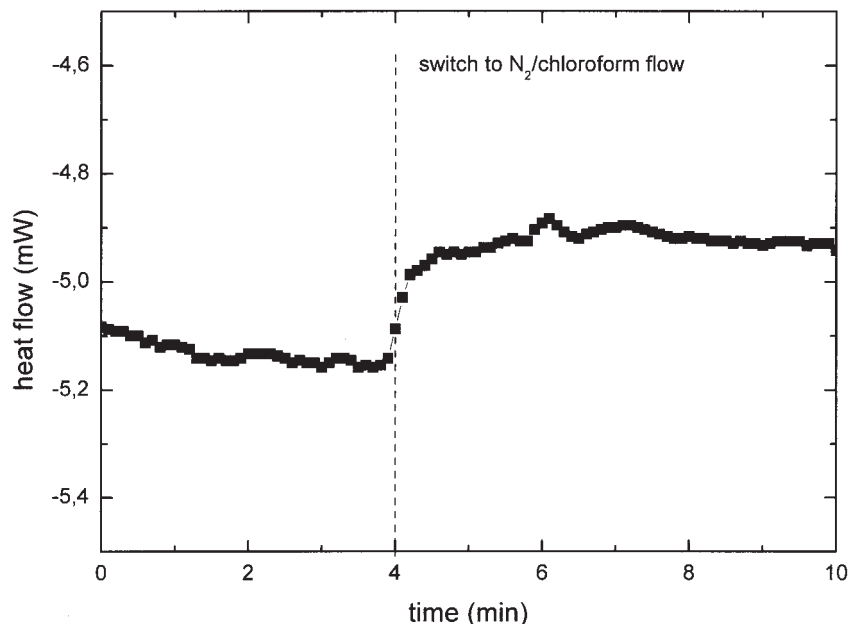
value of  $0.255 \text{ J/g}_{\text{polymer}}$  has been calculated) compared to dissolution enthalpy associated to chloroform sorption.

To correctly evaluate the chloroform sorption enthalpy from calorimetric tests, proper baseline and integration limits have to be defined. Due to the change of the gas environment in the cell oven and of the specific heat of the sample during sorption, it is difficult to define the proper baseline. For this reason, two different procedures based on a different evaluation of the baseline have been adopted: a horizontal-left baseline (i.e., a baseline corresponding to the con-



**Figure 7** Illustration of baseline evaluated taking as reference the constant heat flow reached when the equilibrium value of weight has been achieved.





**Figure 8** Results of the tests performed in the absence of any sorption process by using alumina powder in both the sample and reference pans.

stant heat flow reached before chloroform exposure, see Fig. 6) and a horizontal-right baseline (i.e., a baseline corresponding to the constant heat flow reached when the equilibrium value of weight has been achieved, see Fig. 7). Blank tests performed in the absence of any sorption process by using alumina powder both in the sample and reference pans (see Fig. 8) showed that a heat flow jump is associated to the introduction of chloroform into the oven, suggesting that the choice of a horizontal-right baseline would be the most appropriate.

The specific chloroform sorption enthalpy has been consequently evaluated from the area under the heat flow curve and the equilibrium sample weight increase as measured by TGA. Table I shows the sorption enthalpies calculated by following both integration procedures ( $\Delta H_1$  and  $\Delta H_2$ , respectively) from a set of three tests performed at temperatures close to the average temperature at which the gravimetric sorption tests have been performed (47°C). The mean

values (341 and 342 J/g) obtained by the calorimetric method with the two different baselines are lower than those determined on the basis of the equilibrium sorption data, that is, 500 J/g. The observed difference is likely due to the fact that part of the heat of sorption is released to the gas stream conveying chloroform vapor to the DSC cell. It is not straightforward to take into account this effect through calibration procedures, since it is expected to depend upon sample geometry (e.g., powder, platelet) and characteristic dimension.

## CONCLUSIONS

Sorption of chloroform vapor in semicrystalline syndiotactic polystyrene with nanoporous crystalline form has been investigated by coupled gravimetric and calorimetric methods. The kinetics of chloroform sorption compares well with the evolution of heat of sorption as measured calorimetrically. Nevertheless, comparison of the integral heat of sorption as measured by calorimetry with that evaluated from mass sorption isotherms at different temperatures evidences that the calorimetric procedure apparently underestimates its value, likely due to partial release of exothermic heat to the nitrogen stream conveying chloroform vapor to the sample compartment.

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**TABLE I**  
Weight Gain and Sorption Enthalpies Calculated per Gram of Sorbed Chloroform Following the Two Different Inegration Procedures

Test #	Temperature (°C)	$\Delta H_1$ (J/g)	$\Delta H_2$ (J/g)	Weight gain
1	39	340	346	0.051
2	44	354	357	0.042
3	47	332	320	0.038
Mean value		342	341	

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