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A Rychkov, A Melnikov, A Rodygin, D Anokhin, M Rosenthal, et al.. Ultra-fast chip calorimetry accessories for in operando structural studies of nanogram-sized samples. IOP Conference Series: Materials Science and Engineering, IOP Publishing, 2019, 525, pp.012047. 10.1088/1757-899X/525/1/012047 . hal-03095930

HAL Id: hal-03095930

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Submitted on 4 Jan 2021

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To cite this article: A A Rychkov *et al* 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **525** 012047

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Ultra-fast chip calorimetry accessories for in operando structural studies of nanogram-sized samples

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Abstract. Ultra-fast chip calorimetry is a modern thermal analysis technique based on MEMS-type sensors, which allows performing quantitative measurements on samples of only a few nanograms. However, calorimetry alone is sometimes insufficient for in-depth analysis of complex phase transitions occurring during the experiment. Therefore, in-operando structural analysis was found to be helpful in deciphering the nature of the corresponding structural transitions. Here we report on design of accessories for in-operando synchrotron-based X-ray scattering experiments at low temperatures as well as under different atmospheres and humidities. The examples of applications in polymer physics include analysis of the double-melting behavior of poly(trimethylene terephthalate) and structure formation processes in isotactic polypropylene.

1. Introduction.

Since its introduction in the beginning of the 90s, the technique of ultrafast chip calorimetry, or nanocalorimetry, [1-3] has been attracting a steadily growing interest of a broad scientific community working in various fields materials' science. The main technological breakthrough of ultrafast chip calorimetry compared to the classical methods of thermal analysis is in its use of a MEMS-based measuring cell, which provides the possibility of carrying out experiments at extremely fast heating and cooling rates. The achievable rates can be up to one million times faster than the ones used in the classical DSC. This feature imparts to the novel technique the sensitivity to very small sample sizes of about several nanograms. The new applications of ultrafast chip calorimetry include but are not limited to ultra-thin organic and inorganic films and individual polymer single crystals [4-6]. However, quite often the complexity of the processes occurring during thermal experiments require additional information in order to be fully comprehended, as calorimetry alone can be insufficient to fully clarify the situation. Therefore, it is beneficial to couple the technique of ultrafast chip calorimetry to other in-situ methods of physical-chemical characterization. To this end, we designed a custom-built



nanocalorimeter allowing for in-operando combination with synchrotron-based X-ray scattering experiments [7]. The nanocalorimetric device is compatible with various MEMS chips produced by the Xensor company [8]. The combination of nanocalorimetry and X-ray scattering with fast detection allows simultaneously addressing the thermal and structural parameters of the samples, which simplifies the analysis of the thermal events observable in the nanocalorimetric traces. For example, we revisited the so-called double-melting behavior of semirigid-chain semicrystalline polymers [9-10]. It is well documented that the semirigid-chain semicrystalline polymers can exhibit two and more melting peaks in the heating traces. This phenomenon is not always related to polymorphism and can be observed even for polymers possessing only one crystal modification. In the ongoing debate in the literature, the presence of several melting peaks was necessarily associated with reorganization during heating. However, in order to understand the details of the structure formation processes a combination of nanocalorimetry with in-situ X-ray scattering was badly needed.

In our recent publication, we explored the reorganization behavior of a typical semirigid-chain semicrystalline polymer using such combination of techniques [11]. We showed that the critical heating rate above which all reorganization processes cease to exist can be higher than 1000 °C/s, depending on the crystallization conditions. Therefore, the researcher has to be aware of the critical heating rate corresponding to each set of sample preparation conditions in order to completely exclude the reorganization processes during the experiment. This is obviously a prerequisite for acquiring meaningful thermoanalytical data that reflects the initial sample state and not just the interplay of the reorganization processes (i.e., recrystallization and subsequent melting) occurring during heating ramps. In the present work, we report on development of environmental variable-temperature stages for nanocalorimetric sensors which are compatible with optical microscopy operating in reflection and transmission and synchrotron-based X-ray scattering.

2. Devices designed for experiment.

To extend the operating temperature range of the the custom-designed nanocalorimeter, a low-temperature sensor stage and a prototype of the device were developed. The operation of the stage is based on liquid cooling and uses the thermoelectric Peltier converters. Due to the use of special clamps, a rigid fixation of the nanocalorimeter chip and immobility during thermal expansion of its structural elements is achieved, which is especially important for structural studies. The low-temperature stage also allows using an additional (reference) nanocalorimeter sensor, i.e. a differential setup, to subtract the addendum heat capacity (baseline), which is necessary for quantitative processing of the experimental data.

Figure 1 shows the scheme of the device with indication of the main structural elements. The left panel provides the view with spaced parts, while the right panel is the view of the stage assembly.

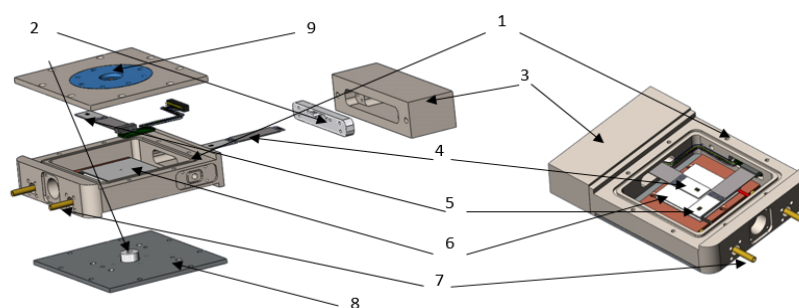


Figure 1. General view of the low-temperature stage for the nanocalorimetric sensor: 1 - housing of the stage, 2 - ceramic thermal screens, 3 - flange with a block of nanocalorimetric sensors, 4 - chip with the sample under study, 5 - reference chip, 6 - Peltier element, 7 - liquid cooling tubes, 8 - invar alloy cover, 9 - silicon nitride window.

The low-temperature stage was combined with X-ray scattering at the micro-focus ID13 beamline of

the European Synchrotron Radiation Facility (ESRF) in Grenoble (France). An additional gaseous nitrogen blowing system was implemented for some elements of the setup, eliminating the possibility of condensation of moisture from the atmosphere. Figure 2 shows the scheme and photo of the experimental setup installed at the ID13 beamline. The implementation of the low-temperature stage made it possible to conduct combined nanocalorimetric and structural experiments in the temperature range from -25 to 400 °C, as well as using the modes of ultra-fast controlled quenching of samples up to 10 000 °C/s.

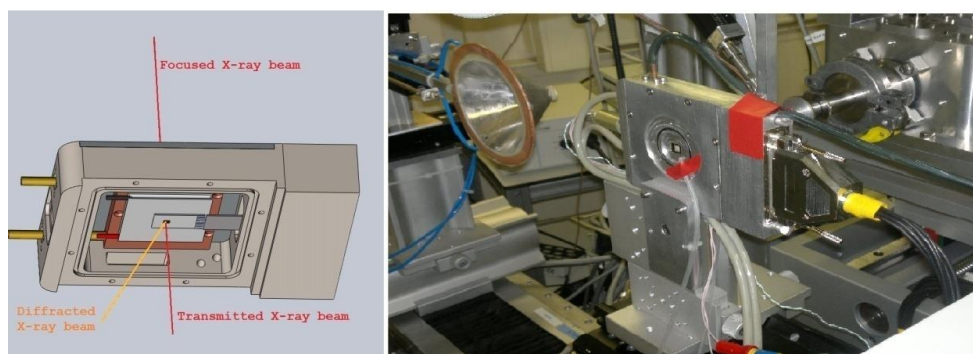


Figure 2. Schematics and photo of the environmental variable-temperature stage for the nanocalorimetric sensor integrated in the ID13 microfocus beamline of the ESRF (Grenoble, France).

The small size of the nano-calorimeter sensor makes it rather straightforward to create special environmental conditions around the chip. In particular, we developed a sealed cell with controlled humidity and atmosphere surrounding the sensor (Figure 3). The cell is connected to the electronic interface of the nanocalorimeter. The humidity inside the cell is controlled by regulating the flow of dry and wet gases into the housing of the chip independently and by mixing them inside the housing. The relative humidity values are measured by the Sensirion SHT31 electronic humidity and temperature sensor. The humidity sensor provides high accuracy and rate of relative humidity measurements and is equipped with a thermocouple, which makes it possible to synchronize the sensor's readings with the signals of the nanocalorimetric sensor. To optimize the cell for X-ray scattering experiments the cell is made prismatic, with two side windows of thin silicon nitride, which is an X-ray transparent material. The model of the assembled cell is given in Figure 3.

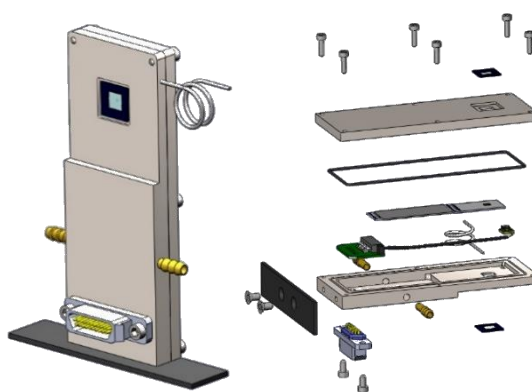


Figure 3. 3D model of the nanocalorimetric chip housing with controlled humidity.

The developed nanocalorimetric accessories make it possible to carry out a wide range of in-operando experiments using different sample geometries such as thin films, fiber microfragments, powder microparticles, etc. In the following of the article we will provide two examples of combined calorimetric and structural studies performed on poly(trimethylene terephthalate) (PTT) and on isotactic

polypropylene (iPP).

3. Experiments and results. The processes of structure formation and melting of semi-rigid chain polymers was elucidated using the example of a typical aromatic polyester, PTT. In the past, low-heating-rate synchrotron experiments and modelling of the semicrystalline structure of PTT [12] allowed concluding that the double-melting behavior is intrinsic to the thermodynamics of this and similar systems. Using modelling of the variable-temperature small-angle X-ray scattering curves with a generalized paracrystalline model it was concluded that the thermodynamic stability of PTT crystals depends not only on their thickness but also on the size of the amorphous gaps with the neighboring crystalline lamellae. The crystallization process at its later stage results in a build-up of negative pressure [12] imposed on the dominant crystals by the later grown subsidiary crystals. This in turn lowers down the melting point of the crystals according to the Clapeyron-Clausius equation. During heating, the melting process starts from the crystals squeezed in the smallest amorphous gaps where the negative pressure effect is the strongest. After melting of the least stable crystal fraction, the remaining crystals acquire additional stability and melt at a higher temperature. Therefore in this case the double-melting behavior can be accounted for by the complex interaction between the crystalline and amorphous regions and by the metastable nature of the polymer crystals.

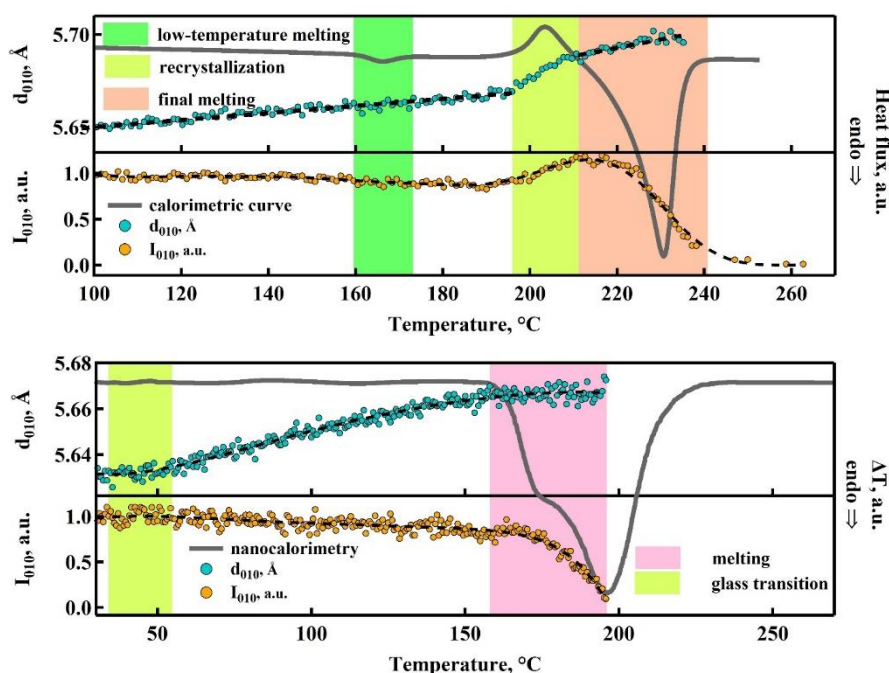


Figure 4. Temperature dependence of the 010 peak position and intensity and the corresponding calorimetric curves for PTT melt-crystallized at 150 °C. The heating rates employed are 1 °C/s (top) and 500 °C/s (bottom). For the sake of clarity the temperature regions of glass transition, as well as low-temperature melting, recrystallization and final melting are highlighted. The calorimetric curve shown in the top panel was measured with a Perkin Elmer 8000 differential scanning calorimeter.

It is noteworthy that in the literature, the double-melting behavior is often interpreted as a sign of reorganization on heating, which is in contrast to our interpretation. In order to clarify this issue, we performed combined in-situ thermal and structural studies of a melt-crystallized PTT at heating rates ranging from 1 °C/s to 3000 °C/s. As an example, figure 4 shows the evolution of position and intensity of the strongest 010 peak of the PTT lattice. The experiment shown in the top panel of figure 4 was conducted at a relatively low heating rate of 1 °C/s. It is noteworthy that at this slow heating rate our custom-built nanocalorimeter is not sensitive to the small sample and was therefore run in the so-called temperature-modulation mode (AC-mode). For the sake of simplicity, we present on the figure a

calorimetric curve measured in the usual DC mode on a conventional Perkin Elmer differential scanning calorimeter (DSC). The displayed DSC curve exhibits low-temperature melting at about 170 °C followed by exothermic recrystallization at ca. 200 °C and eventually the final melting. The structural data confirms that the sample reorganizes on heating. Indeed, simultaneously with the recrystallization peak in the DSC trace one observes a shift of the 010 peak position and an abrupt increase of the peak intensity. This clearly shows that a fraction of new crystals appears at this stage of heating.

The experiment presented in the bottom panel of figure 4 was conducted at a much higher heating rate of 500 °C/s. In this case, the nanocalorimetric curve shows a complex-shaped peak characteristic of the double-melting behavior. At the same time the structural data does not present any evidence for the reorganization processes. Indeed, the 010 peak position gradually shifts upwards due to the thermal expansion whereas the peak intensity reflects melting of the sample. This proves that the double-melting phenomenon is not necessarily coupled with the reorganization of the structure on heating but is inherent to the melting process in such system.

The complex phase transitions in polymer systems can be further illustrated using the example of iPP for which the heating and cooling rate can dramatically affect formation of different phases [cf. e.g., 13]. The left panel of figure 5 shows the nanocalorimetric curves measured during heating of the same iPP sample at 1000 °C/s. The difference between the curves is due to the different initial structures of the sample formed by cooling from the melt at the cooling rates indicated on the figure. It can be seen that for the slowest previous heating rate (i.e. 100 °C/s) the heating curve exhibits just one endothermic event, which can be assigned to melting. For the higher cooling rates the subsequent heating curve becomes more complex: it exhibits a thermal event at ca. 0 °C, as well as the ones at about 90 and 140 °C. The nature of these transitions can be clarified using the wide-angle X-ray scattering (WAXS) profiles measured before each of the heating ramps (cf. the right panel of fig. 5). It can be seen that upon relatively slow cooling from the melt the sample exhibits the semicrystalline state, while for faster cooling rates the crystalline peaks become weaker and eventually disappear leaving first the so-called mesophase state and then a largely amorphous structure. The combination of nanocalorimetry and in-situ WAXS makes it possible to evaluate the critical cooling rates at which the different sample states will be generated. This information is also helpful for understanding of the sample transformation on heating. Indeed, the fully crystallized samples, i.e. the ones corresponding to the slowest previous cooling rates, will undergo melting. For the higher cooling rates, the initial state of the sample is partly mesomorphic, which is visible for example for the WAXS profile corresponding to the previous cooling rate of 300 °C/s. This would explain a more prominent glass transition (the T_g of amorphous iPP equals -7 °C). The thermal event in this region includes a step in the heat capacity due to devitrification followed by an endothermic peak of the so-called thermal ageing. The second endothermic peak in the curves at about 90 °C, which becomes visible already above the previous cooling rate of 100 °C/s stands for the mesophase crystallization, whereas the final melting temperature stays invariable. The enhancement of the glass transition at the highest previous cooling rates reflects the formation of a largely amorphous sample, i.e. at these cooling rates the formation of the mesophase is bypassed.

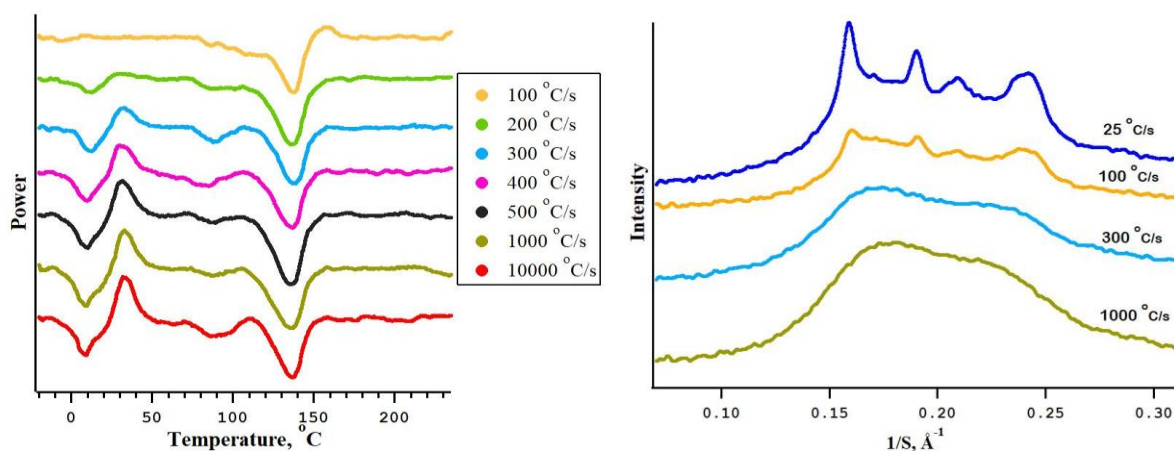


Figure 5. Left: Nanocalorimetric curves corresponding to iPP samples cooled down at different rates (indicated). The measurements were performed at 1000 °C/s. For the sake of clarity, all the curves are shifted vertically. Right: Wide-angle X-ray scattering profiles measured on the samples before starting the heating ramps. For the sake of clarity, the WAXS curves are shifted vertically.

In conclusion, the developed accessories for in-operando nanocalorimetry open a wide range of possibilities for conducting experiments under different atmospheres (including vacuum) and at different humidities. The compact design of the sensor stages equipped with high-quality transparent windows for visible light and X-ray beams make them compatible with the environment of the micro- and nano-focus synchrotron X-ray beamlines. The examples of the measurements provided in the paper show that this technique is useful for studies of polymer samples exhibiting complex thermal transitions on heating and cooling. The combination of such in-situ methods provides unique opportunities for advanced thermal and structural characterization of organic and inorganic samples under various atmospheric conditions.

Acknowledgements

The authors acknowledge the Ministry of Science and High Education of the Russian Federation [contract No.14.616.21.0072 from 28 July 2016 (RFMEFI61616X0072)] for financial support. This work was performed in accordance with the state task no. 0074-2019-0014. The authors are grateful to Manfred Burghammer (ESRF) for excellent technical support at the beamline and fruitful discussions.

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