

Ultra-fast isothermal calorimetry using thin film sensors

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Abstract

A new application of an ultra-fast thin film calorimeter is described. A commercially available sensor, thermal conductivity gauge TCG-3880 (Xensor Integrations, NL) was utilized as a measuring cell for isothermal calorimetric measurements. The sensor consists of a thin membrane (500 nm) with a semi conducting heater and a semi conducting thermopile, which are produced using integrated-circuit (IC) technology. To allow fast scanning sample size should be small too. Samples with masses of about 100 ng were measured.

Different modes of operation were realized: (i) temperature scans over hundreds of Kelvin with rates up to 10,000 K/s; (ii) isothermal heat flow measurements with a time resolution of a few milliseconds; (iii) ac-mode for heat capacity measurements in the frequency range from 1 to 140 Hz at scanning or isothermally. In contrary to classical ac calorimeters beside heat capacity enthalpy changes can be monitored simultaneous.

All these modes can be combined to realize experimental conditions needed to follow isothermal processes in time. As an example, we present isothermal crystallization experiments for fast crystallizing polymers. Heat flow as well as heat capacity was measured after quenching the sample from above the melting temperature to the crystallization temperature. Crystallization kinetics for polycaprolactone (PCL) and polyethylene (PE) are presented in a wide temperature range. We were able to follow isothermal crystallization of PCL in the whole temperature range between melting and glass transition.

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1. Introduction

Due to significant progress in integrated-circuit (IC) technology over the last years thin film calorimetric devices were developed successfully [1–3]. Commercially available calorimetric thin film sensors consist of a silicon membrane of a few μm , e.g. [4]. The heater and the thermometer necessary for calorimetric applications are produced by micro fabrication technologies, e.g. as deposited thin metal films [1] or semi conducting areas in the membrane [4]. Because of the dramatically reduced heat capacity of the addenda such calorimeters allow the measurement of thin films down to nanometer thickness. Specific heat measurements of such samples are important for the characterization of modern materials which as thin films show properties different from the bulk material. Examples include multilayer structures,

many amorphous materials, and ultra-thin films of reduced dimensionality.

On the other hand, such small sensors give us the possibility to achieve extremely high temperature scanning rates. A lot of modern materials are rapidly cooled during production. Such fast cooling often yields non-equilibrium states, which depend strongly on the way the matter came into this state. Therefore, high cooling rates are needed to model these processes in a calorimeter. Injection molding of a polymer or producing of an amorphous metal are examples of such processes.

With conventional differential scanning calorimeters (DSC) one can heat/cool the sample at rates up to 60 K/min (1 K/s). Pijpers et al. [5] have shown that one can use DSC at rates of up to 500 K/min (ca. 10 K/s). This is, however, not high enough to study polymer crystallization at conditions comparable to injection molding [6–8] or to get amorphous metals [9]. There are several approaches to reproduce the cooling rates of such processes. One can rapidly move the sample from a hot into a cold section of the measuring system, cooling rates of several hundreds of K/s can be reached

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[10] or one can measure the temperature of the polymer in an injection molding system [11]. But these techniques do not allow measuring sample properties during fast cooling—they only monitor the process. To measure heat capacity at solidification during fast cooling allows studying crystallization or glass transition in a quantitative way [12].

To reach high cooling rates in calorimetry, it is necessary to reduce heat capacity of the sample and the sensor (sample support, thermometer, heater, wires) dramatically. Nowadays thin film technology offers the possibility to reduce heat capacity of the addenda as needed. Delinger et al. [1] have developed a calorimeter with a heat capacity of the addenda as small as 4×10^{-6} J/K at room temperature, which corresponds to ca. 2 μ g of a polymer. A radical increase in heating rate was achieved by Allen et al. [3] with a thin-film calorimeter allowing heating rates up to 1,000,000 K/s. They use a 30 nm thin sensor with a metal film heater, which is simultaneously used as a thermometer [13]. To get reliable results one has to apply a very stable, low noise current to the heater, thus measurements on heating with such high rates are realized so far only. Vacuum surrounding used to get quasi-adiabatic conditions also prevents fast cooling.

To be able to measure specific heat during fast cooling, we gave up adiabatic conditions and perform measurements in a gas. Moreover, helium surrounding with a six times large thermal conductivity compared to air can be used to achieve highest cooling rates. To get rid of the heating due to the current through a resistive thermometer a thermopile is used. A sensor with separated heater and thermometer, consequently, does not need highly stable currents to drive the heater. Also the output signal of the semi conducting thermopile is relatively large (millivolt), so the requirements regarding electronics in our setup are not as high. As a result, cooling (as well as heating) rates of more than 10,000 K/s can be achieved, for details see [12].

Because the thin film calorimeter [12] allows for fast cooling the question arises if the same instrument can be used to study isothermal processes just after fast cooling. In this paper, we describe a setup to measure enthalpy and heat capacity changes at isothermal conditions. The time resolution is better than 10 ms and the system can be applied to study isothermal crystallization or chemical reactions in a time window not accessible for calorimetric studies before. The capability of the system is demonstrated at the example of isothermal polymer crystallization after quenching from the melt.

2. Experimental

To study fast isothermal processes, one needs to change temperature rapidly to avoid starting the process on the way to the isothermal state. In case of isothermal crystallization, one has to heat up the sample above the melting temperature, and then to quench it to the crystallization temperature and after that to record the measured parameter as a function of

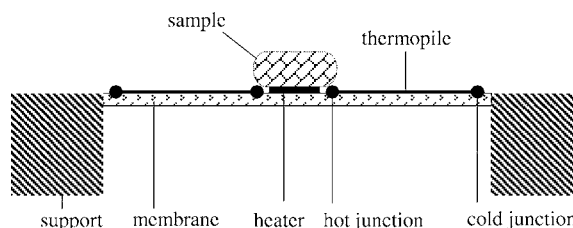


Fig. 1. Schema of the sensor (not to scale).

time. To perform such a measurement we need: (i) a large temperature range—more than 100 K; (ii) a high cooling rate; (iii) a high time resolution, especially at the beginning of the isotherm.

For high heating/cooling rates the temperature gradient inside the sample becomes large. For example, if the heating rate is $dT/dt = 5 \times 10^3$ K/s for a polymer with thermal conductivity of 0.2 W/(mK) and a thickness of 10 μ m a temperature gradient of about 5 K appears [12]. Consequently, a sample thickness of 3 μ m is needed to reduce the gradient to 0.5 K. On the other hand, if we want to measure such thin samples, the thickness of the sensor should be smaller, otherwise the addenda heat capacity will determine the time constant of the system.

2.1. Sensor

As shown in [12,14] a vacuum gauge TCG-3880, Xensor Integration, NL [4], is suitable for fast calorimetric measurements. The sensor consists of a thin SiN_x membrane (thickness ca. 500 nm, size 1 mm \times 2 mm). A heater and the hot junctions of a semi conducting thermopile are located in the membrane center, see Fig. 1. The cold junctions are on the edge of the membrane close to the support. If a current flows through the heater, the thermopile measures the overheating of the middle part of the membrane against the ambient temperature. Here, it is assumed that the temperature of the cold junctions of the thermopile equals ambient temperature. This constant overheating is originally used for the measurement of gas thermal conductivity which depends on pressure (vacuum gauge).

The sensor was placed into a temperature-controlled oven, see Fig. 2. A vacuum shielded oven originally designed for an ac calorimeter [15] was used for all experiments. The internal volume can be filled with some gas at controlled pressure between 10 Pa and 100 kPa. The whole construction fits into a Dewar vessel with liquid nitrogen for cooling. A thin wire Cu-Constantan thermocouple was located close to the sensor to measure surrounding gas temperature. The thermopile cold junction temperature was assumed to be equal to the measured gas temperature.

2.2. Method

A small piece of the material under investigation was placed on the center of the membrane, see Fig. 1, and

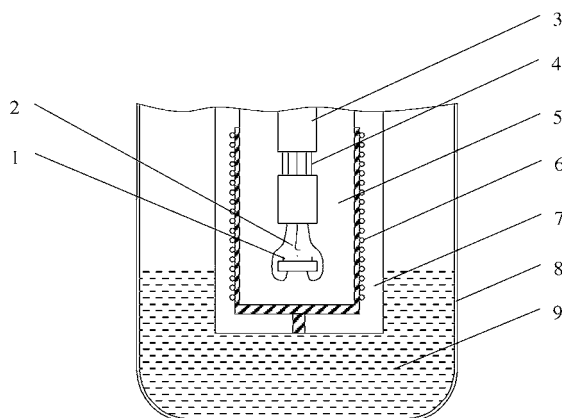


Fig. 2. The oven of the calorimeter (not to scale). (1) sensor; (2) thermocouple to measure gas temperature; (3) thin wall tube; (4) connector; (5) internal volume (pressure controlled); (6) heater; (7) external volume (vacuum); (8) Dewar vessel; (9) liquid nitrogen.

a voltage scan was applied to the heater. Linear heating and cooling with relatively large amplitude were performed. Since the heater resistance is constant in first approximation, we apply a voltage according to square root of the time to get essentially linear heating/cooling. Fig. 3a represents typical time dependencies of the current through the heater. Sample temperature, Fig. 3b, is measured by the thermopile and recorded simultaneously with the heater current.

The derivative of the temperature signal, the heating rate, Fig. 3c, is an essential quantity for the calculation of sample heat capacity [12]. For example, the bend in heating rate close to the end of the heating on Fig. 3c corresponds to the melting of the sample.

To achieve high cooling rates one can use helium surrounding with high thermal conductivity (157 W/(m K) versus 26 W/(m K) of air at room temperature [16]). This way we get cooling rates higher than 10,000 K/s. In Fig. 4, ballistic cooling after switching off the heater power is shown as an example.

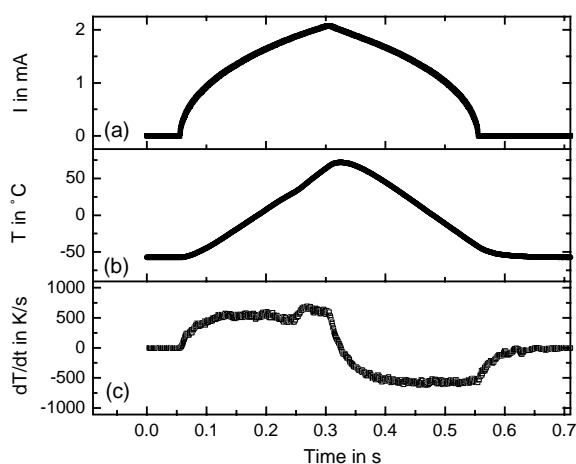


Fig. 3. Measured data for a heating/cooling scan. (a) Electrical current through the heater; (b) sample temperature; (c) heating rate. Sample: PCL ca. 100 ng; oven temperature -58°C .

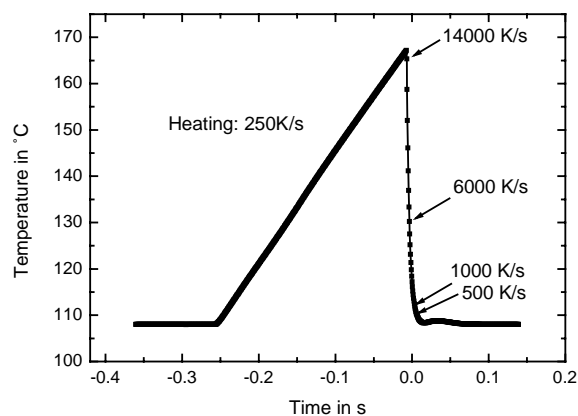


Fig. 4. Temperature vs. time for controlled linear heating and free cooling after switching off the heater power. The local rates are indicated at different temperatures. Surrounding: helium at a pressure of 5 kPa; gas temperature 108°C . Sample: polyethylene ca. 100 ng.

As shown in [12] heat capacity can be obtained from the data shown in Fig. 3. On the other hand, fast heating and cooling can be used to prepare a sample with a certain thermal history as it is needed for isothermal crystallization measurements. For example, one can melt the sample, rapidly cool down to the crystallization temperature and then follow isothermal crystallization, as shown in Fig. 5. This is possible because there is only a very small delay, ca. 10 ms [12], between the power and the temperature. This indicates quasi-static conditions of heating and cooling at such high rate of 700 K/s.

At the end of the cooling, the heater power equals zero. Because of the ballistic cooling at the very end of the cooling scan sample temperature approaches the oven temperature at slower rate. If we zoom in the temperature signal, insert in Fig. 5, we can see some increase of the temperature at the beginning of the isotherm. This is due to the crystallization of the PCL sample, which is an exothermic process. To obtain the heat flow rate to the surrounding from the measured temperature increase one can make use of the almost linear dependency between the heater power and the temperature as seen in Fig. 5. This is because power losses are at the first approximation proportional to the temperature difference between the sample and the surrounding. Details of the calibration are given in [12].

This experiment shows that it is possible to follow isothermal processes utilizing the thin film calorimeter [12] based on the thermal conductivity gauge TCG-3880, Xensor Integration, NL [4]. Additionally, it shows that we are able to prevent crystallization of the PCL sample on cooling. Crystallization at -38°C is below the temperature of the maximum crystallization rate, see Fig. 11 below. At lower temperatures, the crystallization rate decreases dramatically until it reaches zero at the glass transition temperature, see Fig. 11 below. At low crystallization rates, the heat flow rate from the sample to the surrounding decreases too and reaches the noise level. To follow the isothermal process under such conditions, one does not need a calorimeter with

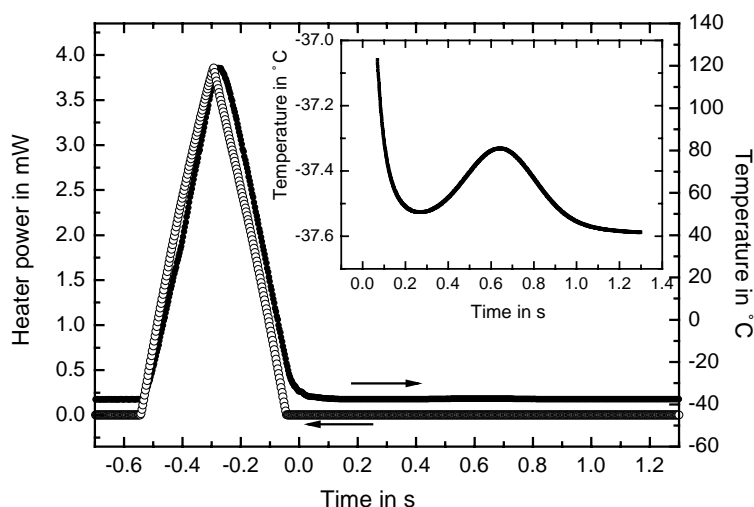


Fig. 5. Melting and isothermal crystallization of a PCL sample, ca. 100 ng. Heating/cooling rate 700 K/s; oven temperature -38°C . Insert shows small temperature change due to crystallization.

high resolution in time. But in order to reach the crystallization temperature without crystallization on cooling we are in need of the fast cooling capabilities of the thin film calorimeter and the thin sample. Therefore, it would be of interest to follow crystallization, as an example, by measuring heat capacity, which is decreasing with increasing crystallinity [17–19].

To measure heat capacity one can apply a small oscillating voltage to the heater to generate an oscillating power of a few microwatts and detect the amplitude of the temperature oscillations on the second harmonic of the voltage [20] as commonly done in ac calorimetry. The measured temperature signal is shown in Fig. 6. The non-sinusoidal shape of the signal (large first harmonic) can be explained by the semiconductive nature of the heater contacts. As generally known from ac calorimetry, the proper choice of the modulation frequency is important if one wants to measure absolute values of heat capacity [21,22]. To study crystallization kinetics, it is enough to measure relative changes in heat

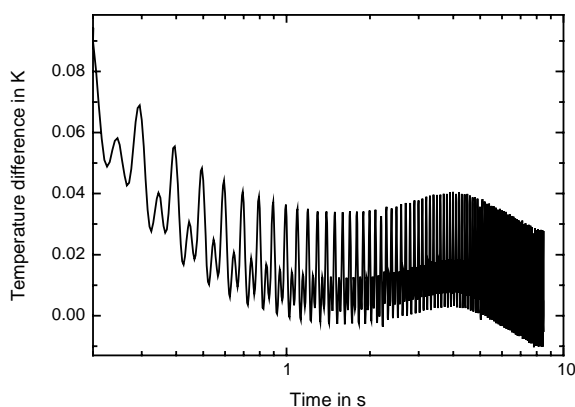


Fig. 6. Temperature signal during quasi-isothermal ac-measurements after quenching the PCL sample from the melt. Gas temperature $T = -54^{\circ}\text{C}$, $2f = 20\text{ Hz}$, results see Fig. 9 below.

capacity and therefore we neglect all calibrations and corrections [20]. Choosing small temperature amplitudes allows keeping conditions of linear response. Then apparent heat capacity can be obtained from the ratio of temperature and power amplitudes. In this mode, we can follow the long-term change in sample heat capacity during crystallization, see Fig. 9 below.

2.3. Electronic

The scheme of the electronic setup is shown in Fig. 7.

A Stanford Research DS340 programmable arbitrary function generator was used to drive the current through the heater in accordance to the desired time–temperature profile. The function was generated by a computer and downloaded to the DS340 via computer interface.

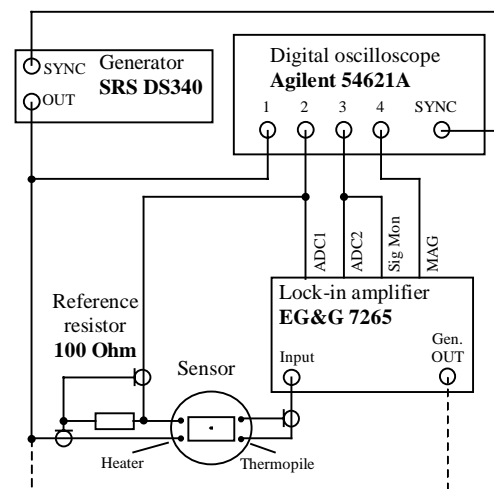


Fig. 7. Scheme of the experiment. Most of grounding as well as temperature control and computer connections are not shown for simplicity. Actually the oscilloscope has only two signal inputs so only two of the four signals (normally 2 and 3) were connected during a single measurement.

Model 7265 lock-in amplifier from EG&G Instruments (now Signal Recovery) was utilized to detect a signal from the thermopile (mostly preamplifier part was used in this mode). “Signal monitor” output was connected to one analog-to-digital converter (ADC) of the 7265 (one gets an effective resolution of 13 bits). Actual gain factor of the preamplifier was calibrated for each gain setting. The other ADC was used to measure the current through the heater. A 100 Ω resistor was connected in series with the heater. The heater resistance itself is about 600–700 Ω depending on temperature. Readouts of both ADC’s were stored in the 7265’s internal buffer memory in burst mode with a sampling interval between 500 μ s and 5 ms. After the measurement, the data were sent to the computer.

The internal generator of the lock-in amplifier was utilized for the measurements in ac-mode. The lock-in amplifier measured the amplitude of the temperature oscillations at the second harmonic. Heater voltage amplitude was 30 mV, corresponding to power amplitude of about 1 μ W. The voltage at the thermopile was about 30 μ V, corresponding to temperature amplitude of about 30 mK.

Moreover, one can perform “scan” and “oscillating” measurements simultaneously. Then the generator output of the 7265 lock-in amplifier was connected in parallel to the DS340 output (dashed line in Fig. 7). The 50 Ω internal output resistance of each generator resolves the problem of electrical connection of the two outputs. Note that the output voltage should be recalculated because the output resistance of each generator acts as an additional 50 Ω load in parallel with the system (heater + reference resistor).

It was not possible to synchronize the start of data acquisition of the 7265 with the beginning of the pulse of the DS340 because of problems in both devices. If a TTL strobe signal is connected to the “TRIG” logic input of the 7265 AND the unit is programmed to “listen” to this input, a “cross-talk” between “TRIG” and “ADC” inputs is observed. The step in the readout of the analog-to-digital converter is about 13 mV between “Logic 0” and “Logic 1” state of the “TRIG” input. This corresponds to about half of the PCL crystallization peak. Therefore, no synchronization between the generator and the ADC was used.

An additional problem is present in the DS340. The pulse on “SYNC OUT” comes with some delay after the beginning of the waveform generation. A similar delay in all other modes is observed too.

The digital oscilloscope 54621A from Agilent Technologies was used instead. This digital oscilloscope registers the input data all the time and not only after the synchronizing pulse. Therefore, it was possible to record the whole signal completely also before the SYNC signal. This gave a good time reference to the start of the heating. Continuously repeating heating/cooling cycles were performed with a repeat frequency between 0.01 and 0.5 cycles per second. The “averaging” possibility of the oscilloscope was used to improve the signal to noise ratio. Because of the limited resolution of the oscilloscope (8 bit) large temperature scans

(for melting) and small temperature changes (during crystallization) were recorded separately with different settings of sensitivity.

The 54621A was used for ac measurements as well. The ac voltage (e.g. at 70 Hz) from the internal generator of the lock-in was applied to the heater and the lock-in amplifier measured the thermopile signal at the second harmonic. The lock-in was programmed such way that the magnitude (MAG) appears at one of the analog outputs which was connected to the oscilloscope input (4) for averaging.

A Eurotherm 818S controller was used to control oven temperature and a Prema 6001 digital multimeter to measure the thermocouple voltage to get gas temperature. The reference point of the thermocouple was electronically stabilized [15]. A self-made computer program was used to control the instruments.

2.4. Samples

To check the capabilities of the system two samples were investigated. The first one was polycaprolactone (PCL) received from Sigma–Aldrich (order code 81277). A small piece was cut under a microscope and placed very carefully onto the center of the sensor membrane (500 nm only), than a low-frequency electric current was applied to the heater to melt the sample and to fix it on the membrane. At the end, it was a droplet of 60–80 μ m diameter. Sample mass was ca. 100 ng. PCL was measured in air at a pressure of 5 kPa.

The other sample was linear polyethylene (PE) (Standard Reference Material SRM 1484, National Bureau of Standards). The sample was prepared in the same way and has also a mass in the order of 100 ng. Because PE crystallizes very fast helium surrounding at atmospheric pressure was used to get higher cooling rate and to prevent crystallization during cooling as much as possible.

3. Results and discussion

We studied the kinetics of isothermal crystallization of PCL and PE to test the new calorimeter. For relatively fast crystallization, the heat flow rate due to the enthalpy change is large. Then we can observe a crystallization peak in the temperature, see Figs. 4–6, 8. In the time interval between the end of the cooling and the local maximum of overheating, crystallinity reaches roughly half of its end value at the actual temperature. We call this time “crystallization half-time”. The reciprocal is a measure for the overall crystallization rate. Note that only part of the polymer can crystallize, while the rest remains in the amorphous state also after a long time [23].

The crystallization half-time shows the typical bell shaped temperature dependence. The minimum is between melting and glass transition temperature. At these temperatures, crystallization half-time diverges. Only for slowly crystallizing polymers like polyethyleneterephthalate the whole curve

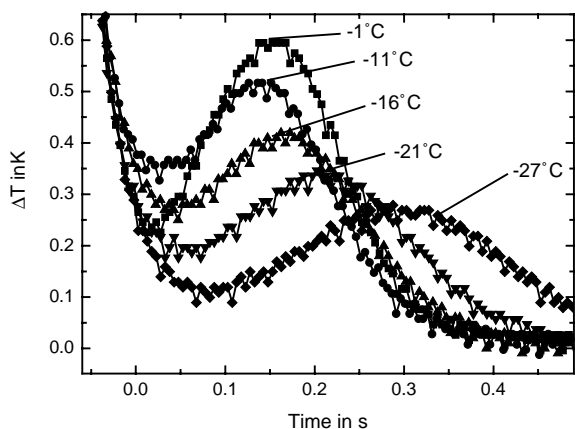


Fig. 8. Isothermal crystallization of PCL at different gas temperatures after heating/cooling at 500 K/s. Air pressure 30 Pa.

can be studied in common DSC's. We have chosen PCL and PE, a fast and a very fast crystallizing polymer, to check the limits of the thin film calorimeter for isothermal measurements. Fig. 8 shows measurements for PCL at temperatures where crystallization half-time reaches the minimum. The shortest time measured for PCL is 140 ms. As can be seen in Fig. 8, the resolution in time of the calorimeter is much better. At temperatures where the crystallization time increases, the peak becomes broader and the peak height decreases, see Fig. 8. Only the area under the peak is nearly conserved because it corresponds to the enthalpy change. At crystallization half-times longer than 10 s the temperature signal decreases below the noise level. To follow crystallization at slower rates we have to switch to heat capacity measurements as described above.

A relatively high oscillating frequency was chosen to get better resolution in time and to follow crystallization almost from the very beginning. The "crystallization half-times" obtained by the two methods, total heat flow and heat capacity,

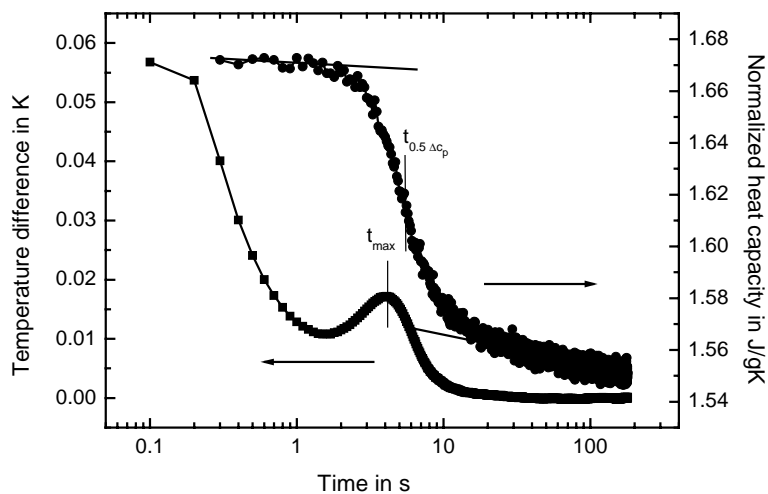


Fig. 9. Different modes of PCL crystallization kinetics measurement. Heat frequency $2f = 140$ Hz, oven temperature -54°C . The curves represent the average over 128 measurements utilizing the oscilloscope.

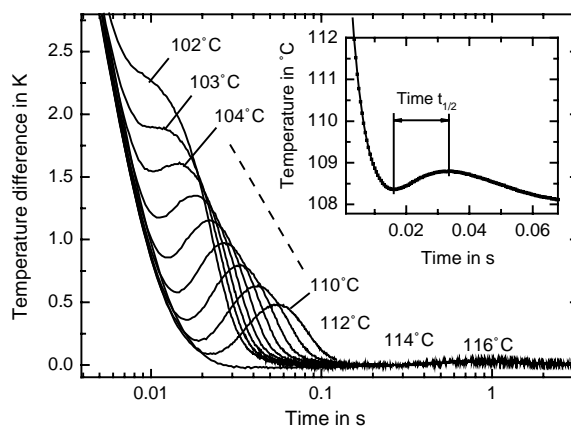


Fig. 10. Crystallization curves for polyethylene (NBS SRM 1484). Indicated temperatures are oven temperatures, corresponding "crystallization temperature" values were less than 2 K different. Insert: definition of "crystallization half-time". Measurement in helium at 5 kPa.

are the same within uncertainty of about 2 ms, see Fig. 9. The time of the maximum of crystallization rate (the local maximum in the temperature signal), t_{\max} , corresponds in good approximation to the time when heat capacity approaches half way of the total decrease, $t_{0.5\Delta cp}$.

Similar measurements were performed with polyethylene. This sample crystallizes much faster; even at the highest cooling rate it was impossible to obtain an amorphous sample below 110°C . Measured temperature traces are shown on Fig. 10. One can see that at temperatures below 110°C crystallization starts already at cooling. Therefore, the lowest value of temperature before the crystallization peak (and not the oven temperature) was assumed to be "crystallization temperature". Next, time of the temperature minimum was assumed to be the "start time". Definition of "crystallization half-time", $t_{1/2}$, is shown on the insert in Fig. 10. For low temperatures, where the temperature even did not reach a minimum (oven temperature 103°C), we did not define a

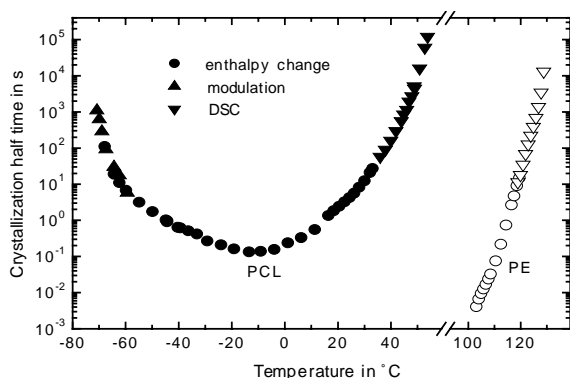


Fig. 11. Crystallization kinetics of PCL (filled symbols) and PE (open symbols). Circles: “enthalpy change” mode; up triangles: modulation mode with chip-sensor; down triangles: DSC measurements (Perkin-Elmer Pyris-1, Setaram DSC 121).

“crystallization half-time”. Nevertheless, time resolution of the thin film calorimeter is below 10 ms.

It is remarkable, that at some temperatures, crystallization occurs so fast, that this prevents the sample from fast cooling to the surrounding temperature. For instance, at oven temperature 102 °C, the remaining overheating is about 2.5 K. So, active temperature control of the sensor should be used for the measurements when the heat produced by the sample influences its temperature significantly.

The results for both samples are summarized in Fig. 11. For PCL, it is possible to study isothermal crystallization in the whole temperature range between melting and glass transition temperature. In other words, we were able to produce an amorphous PCL sample at all crystallization temperatures. For PE, cooling was not fast enough to prevent crystallization on cooling to temperatures below 110 °C. Nevertheless, the temperature range for isothermal crystallization studies is significantly extended to lower temperatures compared to common DSC’s. With DSC’s crystallization can only be followed down to 119 °C but with the thin film calorimeter we reach 103 °C.

4. Conclusions

We present a new application of an ultra-fast thin film calorimeter [12]. The calorimeter allows isothermal measurements with a time resolution better than 10 ms. This allows studying fast processes like crystallization or chemical reactions under conditions relevant in practice. It is possible, as an example, to study polymer solidification at cooling rates and at times occurring during injection molding.

No adiabatic vacuum surrounding was used, just the reverse, heat leakage was taken into account and helium with its high thermal conductivity was utilized as a surrounding gas to get maximum cooling rate of more than 10,000 K/s.

Samples as small as 100 ng were measured to minimize temperature gradients within the system.

Further improvement of the system is possible by active control of the isothermal crystallization temperature at a level above the gas temperature. Much higher cooling rates especially at the end of the cooling process can be realized this way, see Fig. 4. Temperature measurement itself also needs some improvement, because the thermopile sensitivity is not defined exactly.

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