Non Adiabatic Thin-Film (Chip) Nanocalorimetry for Fast (10^5 K/s) Scanning and AC-calorimetry

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Abstract:
Utilizing a thin film chip sensor as a fast calorimeter we are able to extend the scanning rate range of commercial DSC's (10^{-5} K/s to 10 K/s) to rates as high as 100,000 K/s. The gauge is placed in a thermostat with controlled gas pressure and temperature to be utilized as a device for fast scanning and AC-calorimetry of sub microgram samples with sensitivity 1 nJ/K in scanning and pJ/K in AC-mode. The nanocalorimeters are used in combination with conventional DSC in scanning, isothermal, and AC-mode (TMDSC) to study melting, crystallization, recrystallization, and glass transition of polymers and polymer clay nanocomposites.With these sensors we are able to measure at controlled cooling at the same high rates as on heating. Because of the fast equilibration time isothermal experiments can be performed after scanning at several thousand Kelvin per second. The dead time after such a quench is in the order of 10 ms and the time resolution is in the order of milliseconds. These ultra fast calorimeters allow us to study the kinetics of extremely fast processes in semicrystalline polymers. For example, we are able to follow isothermal crystallization of ε-Polycaprolactone (PCL) and isotactic polypropylene (iPP) in the whole temperature range between melting and glass transition.
Heat capacity can be measured in AC mode for sample masses below one nanogram as needed for the study of the glass transition in nanometer thin polymeric films. The calorimeter allows for the frequency dependent measurement of complex heat capacity in the frequency range from 1 Hz to 1 kHz. The glass transition in thin polystyrene and PMMA films (50 – 4 nm) was determined at well defined experimental time scales. No thickness dependency of the glass transition temperature was observed within the error limits (±3 K) - neither at constant frequency (40 Hz) nor for the trace in the activation diagram (1 Hz – 1 kHz).

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