Melting and Reorganization of Polymer Crystals Studied by Fast Scanning Calorimetry (10,000 K/s)

C. Schick[C,S] and A. Minakov
Inst. of Physics, University of Rostock, Rostock, Germany
christoph.schick@uni-rostock.de

Utilizing a thin film gas pressure sensor as a fast calorimeter, we are able to extend the scanning rate range of commercial DSC's (μK/s to 10 K/s) to rates as high as 10,000 K/s. With these sensors, we are able to measure during controlled cooling at the same high rates as during 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 on the order of 10 ms, and the time resolution is on 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. At the maximum crystallization rate, the crystallization half times are 200 ms for PCL and 50 ms for iPP, respectively. The crystallization process can be easily followed in an isothermal crystallization experiment after cooling at 2,000 K/s in order to produce amorphous samples.

On the other hand, the high heating and cooling rates allow us to study the reorganization of semicrystalline polymers during heating. For PET crystallized at 130 °C, reorganization needs less than 40 ms between 150 and 200 °C. At heating rates of 1,300 K/s, where reorganization is prevented, the sample melts in the temperature range 150 to 220 °C. The "main" melting peak at about 250 °C, as always seen in DSC curves, disappears totally. This clearly shows that all crystals formed at 130 °C melt below 220 °C.

We will report about very fast reorganization of nanostructures in semicrystalline materials during heating as well as during cooling, and isothermally utilizing the new calorimetric technique.