

## Differential Scanning Calorimetry

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## Crystallization Temperature vs. Cooling Rate: the Link with “Real-Life” Polymer Processes

### Introduction

A relatively new technology for calorimetry has recently been discussed for practical use and since then marketed by PerkinElmer under the name HyperDSC<sup>®</sup>. The detailed characteristics and use of this new mode of measurement, which represents a major step forward in Fast Scanning Calorimetry (FSC) as compared to Standard DSC, have been published.<sup>1-4</sup> Controlled and constant scan rates of hundreds of degrees per minute and combinations thereof, both in the cooling and heating mode, are possible thanks to the small furnace size compared with the bulky furnace of the conventional heat flux DSC (Figure 1). Thanks to the power compensation design which supports accurate heat flow rate measurement, heats of transition, heat capacities, temperature-dependent crystallinities etc. can be established at the extreme rates applied. The short measuring times also provide the high throughput needed in e.g. combinatorial chemistry.

### PerkinElmer Power Compensation vs. Heat Flux

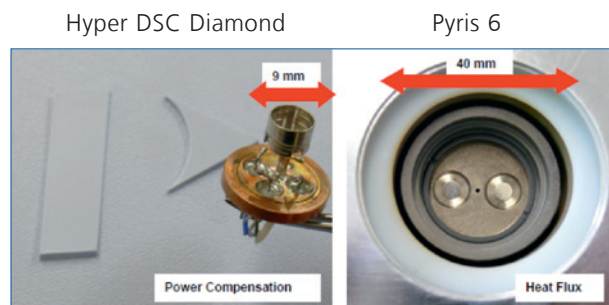


Figure 1. Furnace of HyperDSC versus heat flux DSC furnace.



Application fields benefiting from HyperDSC concern study of the kinetics and metastability of macromolecular and pharmaceutical systems, particularly the analysis of rate-dependent phenomena under real temperature-time conditions. Thus, HyperDSC is very much suited to investigate these systems with respect to their kinetics of processes such as crystallization, cold crystallization, recrystallization, annealing, and solid-state transformations.

Milligram and submilligram amounts of material can be investigated at controlled cooling and heating rates as high as hundreds of degrees per minute, which facilitates the analysis of films, expensive and extraordinary products, inhomogeneities in materials etc.

High cooling rates need to be applied to simulate processing conditions such as in film blow molding, injection molding and extrusion. It appears that for some processing techniques the cooling rate can be mimicked by HyperDSC. Measurements concerning metastability and kinetics are also necessary to (re)connect heating behavior with cooling history.

## Experimental

The PET/PBT samples reported have been supplied by DSM. DSC measurements were performed using a Diamond DSC (PerkinElmer) with an Intracooler II cooling accessory. Cooling rates of 10 to 250 °C/min have been used to study their effect on the crystallization behavior of the polymers involved. To keep the thermal lag minimal, the sample sizes were reduced with increasing cooling rates.

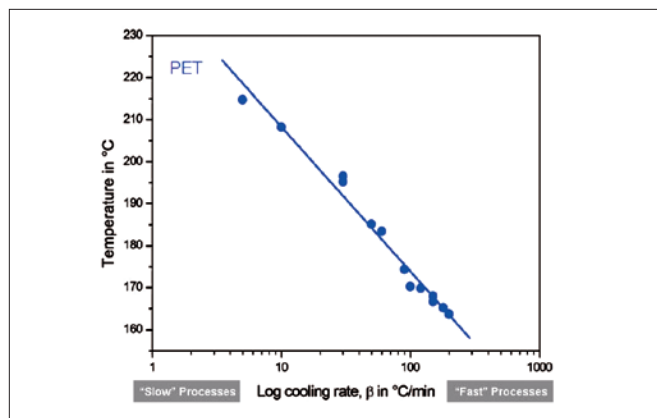


Figure 2. PET crystallization peak temperature as a function of log cooling rate.

## Results and Discussion

In industrial applications the crystallization temperature of a polymer is considered to be the temperature at which the polymer becomes solidified during processing. This temperature

is the limiting value for proper injection molding conditions for “real-life” applications. A polymer or compound which crystallizes “too fast” will solidify too soon resulting in a not-completely filled mold. If the polymer or compound crystallizes “too slow”, the release from the mold will be problematic.

Presenting a characteristic crystallization temperature as a function of the (log) cooling rate provides useful insight into the crystallization behavior of the material studied. Figure 2 shows the crystallization peak temperature of PET vs. log cooling rate. With increasing cooling rates, this temperature decreases significantly.

In case of polyethylene terephthalate (PET) and polybutylene terephthalate (PBT), Standard DSC experiments at relatively slow cooling rates suggest that PET will crystallize prior to PBT. However, when measured during fast cooling by means of HyperDSC it is seen that one should expect that PBT crystallizes first, followed by PET (Figure 3). Thus, it is obvious that in many cases fast scanning represents realistic conditions in practice – like extrusion – much better than the often used low scan rates, like 10 °C/min. Consistent with this awareness the window of analysis of the HyperDSC range of PerkinElmer has been enlarged up to cooling rates of 750 °C/min by way of the recently introduced DSC 8500.

Not only is the sequence of crystallization important but also the crystallizability itself matters: PBT crystallizes at 173 °C while the PET studied here does not crystallize anymore at cooling rates of 225 °C/min and higher. One should consider

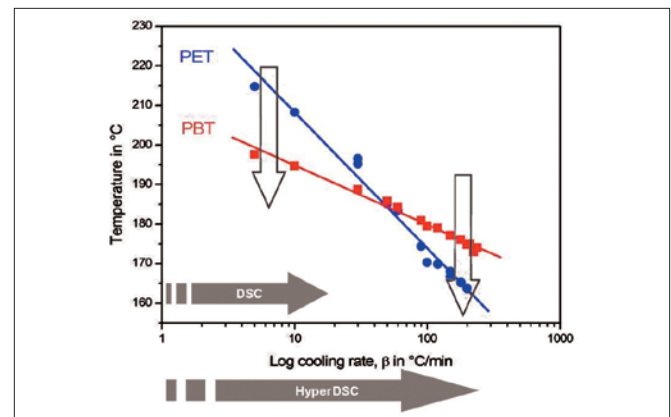


Figure 3. Crystallization temperatures of PET and PBT as a function of log cooling rate.

putting such “right” values into computer-aided industrial design software to improve polymer applications for automotive, shipbuilding, and aerospace industries, industrial and architectural design, prosthetics, and many more.

Thus, HyperDSC should be applied in order to mimic “real-life” processes and industrial processing much better than hitherto has been done. Furthermore, HyperDSC can handle sample masses ranging from approximately 1 µg or less up to more than 10 mg, by which one can choose a representative sample mass.

A special thanks to DSM Resolve and Science & Technology of the Netherlands for their contributions to this application note.

## Conclusions

Since polymer crystallization is significantly influenced by the actual cooling rate, the measurement of a characteristic crystallization temperature should be carried out at the same cooling rates as realized during polymer processing conditions. The conventional 10 °C/min cooling rate represents the low and small part of processing cooling rates applied in practice. Rates usually are much higher, near hundreds of degrees centigrade per minute. Therefore, results from a conventional cooling experiment using a scan rate of e.g. 10 °C/min can be misleading in practice, as illustrated by the PET and PBT case. Therefore, the fast cooling capability of HyperDSC is crucial for mimicking actual polymer processes – such as extrusion – and provides a realistic insight into polymer crystallization behavior. As such, it is an indispensable analytical tool to link experimental data with real-life polymer processes.

## References

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