

APPLICATION NOTE

Polyolefines – DSC 214 *Polyma*



DSC 214 *Polyma* for the Kinetics Analysis of the Isothermal Crystallization of Polyolefines

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Introduction

Until now, isothermal crystallization of polyolefines has not been easy to measure in heat-flux DSCs because of the fast reactions. If the isothermal temperature of crystallization is not achieved fast enough, the polymer crystallizes during cooling. Moreover, an even short temperature undershoot under the programmed isothermal segment would unintentionally induce the start of crystallization. This combination of fast cooling rates and fast equilibration at the target temperature without undershoot made power-compensated DSCs better suited than heat-flux DSCs for this type of measurements.

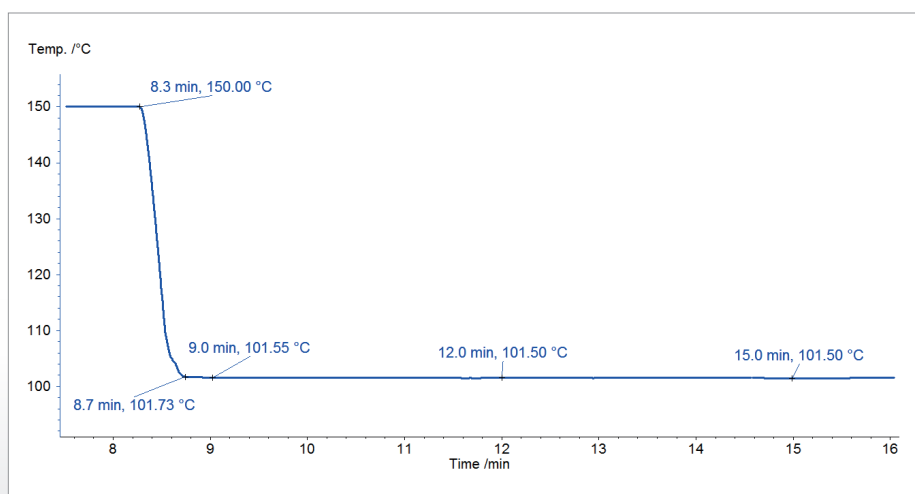
Thanks to the low thermal mass of the *Arena* furnace of the DSC 214 *Polyma*, it is the first DSC that combines robustness

and easy handling of a heat-flux DSC with fast heating and cooling possibilities of a power-compensated DSC.

Isothermal Crystallization of LDPE

The DSC 214 *Polyma* was used to carry out tests of isothermal crystallization at different temperatures on LDPE. Proper regulation parameters were used in order to optimize the transition from a fast cooling to the isothermal segment.

The 3.04-mg sample was heated to 150°C at 20 K/min. After a 2-minute isotherm, the polymer was cooled to eight different temperatures between 101.5°C and 98.5°C, each temperature separated from each other with 0.5°C. The sample was then maintained at the target temperature until the end of the exothermic crystallization reaction.



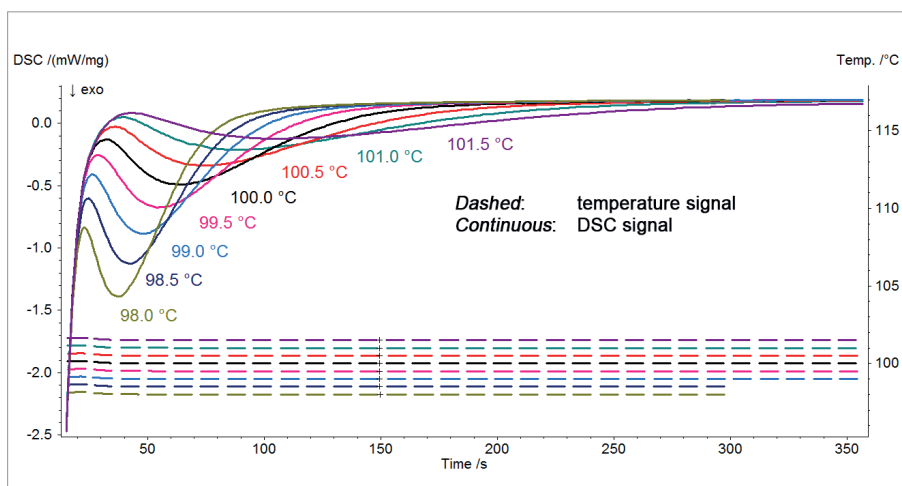
1 Temperature profile of the cooling to 101.5°C

Presented in figure 1 is the temperature profile of the cooling from 150°C to 101.5°C. It shows that the target temperature is quickly achieved without undershoot and that it remains stable during the complete isothermal segment.

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The resulting DSC curve of the isothermal segments at the eight temperatures of the isotherm between 101.5°C and 98.5°C are displayed in figure 2.

The exothermal peak detected during the isothermal segment of the measurements results from the crystallization of polyethylene. As expected, the reaction occurs earlier with decreasing target temperatures. The slope of the peak is higher with decreasing temperature of the isotherm. This is due to a faster reaction rate.



2 Isothermal crystallization of LDPE at 8 different temperatures with the DSC 214 *Polyma*

A difference of only 0.5°C between the temperature of the isotherm leads to big difference in the resulting DSC crystallization curves, indicating a strong influence of the temperature on the reaction. An undershot, even of only some tenths of a degree, would start the reaction unvoluntarily. That is why the temperature must be well controlled during the change from cooling to the isothermal segment.

From DSC Curves to the Determination of the Activation Energy of the Crystallization Reaction

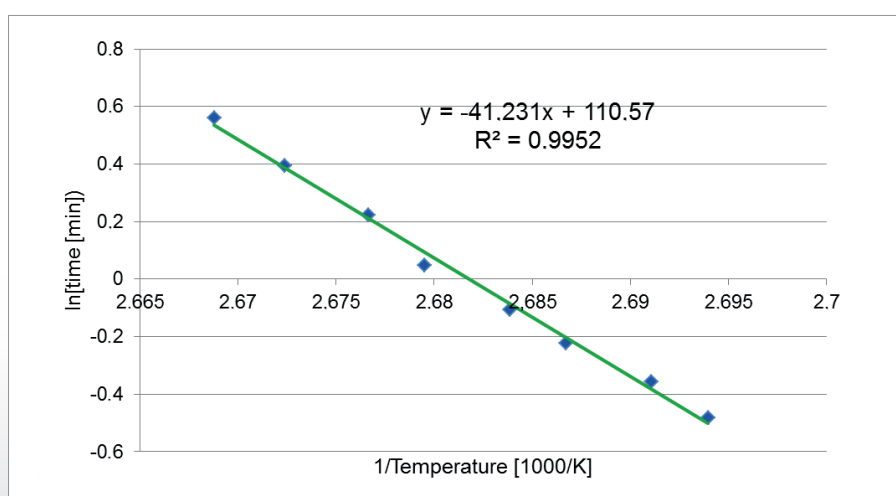
A kinetic study was carried out according to ASTM standard E2070-13 (test method - Time-to-Event), where the lapsed time at a constant conversion and at isothermal

temperature T and the energy of activation E are related to the following equation:

$$\ln[\Delta] = E/RT + b, \text{ where } R = 8.31 \text{ J/(K}\cdot\text{mol)}$$

The slope E/R of the curve $\ln[\Delta t]=f(1/T)$ can be used to determine the activation energy of the reaction.

The time elapsed between the beginning of the isotherm and the peak maximum was determined for each temperature. Each point was plotted in the graph $\ln(\text{time})$ as a function of $1/T$. The slope of the trend line allows for the determination of the activation energy of the reaction. Here, it amounted to 434 kJ/mol.



3 Determination of the activation energy by displaying $\ln(\text{time})$ as a function of $1/\text{temperature}$

Sources:

ASTM E2070-13: Standard Test Method for Kinetic Parameters by Differential Scanning Calorimetry Using Isothermal Modes