



Short communication

Microfocus wide-angle X-ray scattering of polymers crystallized in a fast scanning chip calorimeter

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ABSTRACT

Microfocus wide-angle X-ray scattering (WAXS) has been applied for analysis of the polymorphism of isotactic polypropylene and polyamide 6 prepared in a fast scanning chip calorimeter (FSC). Samples with a typical mass of few hundred nanograms, and lateral dimension and thickness of about 100 μm and 20 μm , respectively, were exposed to a defined thermal history in the FSC and subsequently analyzed regarding the X-ray structure at ambient temperature using an intense synchrotron microfocused X-ray beam. The relaxed melt of isotactic polypropylene was cooled at rates of 40 K s^{-1} and 200 K s^{-1} which allowed formation of α -crystals or mesophase, respectively. Polyamide 6 was isothermally crystallized at 95 $^{\circ}\text{C}$ and 180 $^{\circ}\text{C}$ which led to formation of γ -mesophase and α -crystals, respectively. This study demonstrated, for the first time, that FSC polymer crystallization experiments could be completed and expanded by subsequent in situ structure analysis by X-ray scattering.

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1. Introduction

Non-adiabatic fast scanning chip calorimetry (FSC) for analysis of crystallization, melting and reorganization of polymers has been introduced about a decade ago by the pioneering work of Schick [1,2], and is nowadays considered as a well-established experimental tool for polymer characterization. It allows quantitative calorimetric analysis of phase transitions at rates of cooling and heating up to 10⁶ K s^{-1} [3], depending on the specific sensor and setup used, and the time-resolution in isothermal experiments is of the order of magnitude of milliseconds. Standard differential scanning calorimetry (DSC) permits cooling at rates up to only few hundred K min^{-1} [4–6] which often leads to crystallization at low supercooling. The use of FSC allows bypassing crystallization at low supercooling and enables analysis of structure formation at

high supercooling. Increasing supercooling of the melt leads to an increase of the nucleation density or even change of the nucleation mechanism [7–9], ultimately affecting the morphology and superstructure of the ordered domains/crystals which develop, and materials properties [10–12]. In addition, and more important in the context of the present work, variation of the supercooling of the melt may lead to formation of different polymorphs, as is outlined below on the examples of isotactic polypropylene (iPP) [13], and polyamide 6 (PA 6) [14].

Information about the crystal structure and the polymorphism of crystallizable polymers requires the use of wide-angle X-ray scattering (WAXS). As far as we are aware, no successful attempts have been made to analyze the X-ray structure of polymer samples prepared in an FSC. It is the intention of the present study to demonstrate the advantageous combination of FSC which enables exact control of the nucleation and crystallization pathways and detection of enthalpies and temperatures of transitions, and WAXS for subsequent analysis of the resulting phase structure. Earlier WAXS analyses of the supercooling-triggered polymorphism of polymers were performed on samples prepared in special rapid-cooling devices [15–20], with disadvantages of non-linear cooling, limited maximum cooling rate, decreasing cooling rate on approaching the target temperature, or, more important, impossibility of simultaneous measurement of enthalpies of transitions. With

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the introduction of FSC, these disadvantages on sample preparation are removed; however, since FSC requires the use of specimens of extremely low mass and size, WAXS analysis is not straightforward and requires sophisticated instrumentation, as described and tested in this work.

Furthermore, due to the high surface-to-volume ratio of FSC samples, crystallization may be affected by nucleation of the ordering process at the free surfaces of the sample, or at the sample–membrane interface, but not in the bulk. Comparison of X-ray data obtained on FSC samples and on macroscopic samples of lower surface-to-volume ratio may provide information whether the large specific surface area of FSC samples influences the crystallization process.

In the present X-ray study of the supercooling-controlled polymorphism of polymers, samples of iPP and PA 6 prepared in an FSC were employed. These polymers were investigated in detail in the past regarding the effect of cooling rate/supercooling on the kinetics of structure formation and on the polymorphism. Films with a thickness of about 100 μm were cooled at different rates in home-made rapid-cooling devices, with the evolution of the WAXS structure followed in real time during cooling using synchrotron radiation [18–20], or *ex situ* after completion of the cooling experiment [11,15–17]. In case of iPP it was found that cooling at rates less than about 100 K s^{-1} permits formation of monoclinic crystals while faster cooling to ambient temperature leads to mesophase formation. Similarly, cooling PA 6 at a rate lower than about 10 K s^{-1} allowed development of α -crystals, while faster cooling to room temperature caused formation of γ -mesophase or even full vitrification of the melt. The X-ray studies have been completed by in-depth FSC analysis of the kinetics of crystallization and mesophase formation [21–23], and analysis of the morphology and superstructure of crystals and mesophase [11,24,25]. This notwithstanding, it needs to be emphasized that interpretation of a stand-alone FSC heat-flow rate signal requires complementary knowledge of the phase structure. Most straightforward is the direct WAXS analysis of the FSC sample, after the imposition of a certain thermal history.

2. Experimental

2.1. Materials

We used an isotactic polypropylene PP 531P homopolymer from Sabic (The Netherlands), with a mass-average molar mass and polydispersity of 631 kDa and 5.3, respectively, for microfocus WAXS analysis of the structure after cooling at rates of 40 K s^{-1} and 200 K s^{-1} ; from prior analyses it is expected that cooling at 40 K s^{-1} leads to crystallization while cooling at 200 K s^{-1} causes mesophase formation [15–19,21]. Furthermore, we employed a polyamide 6 Akulon material from DSM (The Netherlands) with a mass-average molar mass of 33 kDa and a polydispersity of 2. The PA 6 sample was isothermally melt-crystallized at temperatures of 180 $^{\circ}\text{C}$ and 95 $^{\circ}\text{C}$, with the intention to allow formation of α -crystals and γ -mesophase, as reported in the literature [26].

2.2. Instrumentation

2.2.1. Microfocus wide-angle X-ray scattering

Microfocus wide-angle X-ray scattering experiments at ambient temperature on samples placed on an FSC sensor have been performed at the BM26B (DUBBLE) SAXS/WAXS beamline at ESRF in Grenoble (France) [27]. The synchrotron beam was focused at the sample position by a post-focusing Kirkpatrick-Baez system consisting of two orthogonal coated silicon substrates bent into elliptical shapes. The horizontal and vertical beam dimensions at

the sample were adjusted to 20 μm and 15 μm , respectively, in order to achieve maximum signal to noise ratio. The wavelength of the X-rays was 0.1033 nm, and the sample to detector distance was 252 mm. We used a 2D Frelon CCD detector with an active area composed by 1024 \times 1024 pixels and a pixel size of 94 μm \times 94 μm . The accumulation time was 60 s for all samples. The X-ray images were corrected for dark current and background scattering. Calibration of the angular range has been achieved by using standard α Al_2O_3 and HDPE samples. The background was provided by an image taken in the center of the empty/unloaded reference calorimeter of the FSC sensor used. The FSC sensors were carefully aligned perpendicularly with respect to the micro X-ray beam using high precision motorized stages. After pre-alignment of the FSC sensors using a high magnification optical camera, the small samples were aligned with respect to the X-ray beam using a high resolution horizontal and vertical grid scan while monitoring the scattered intensity at the WAXS detector.

2.2.2. Fast scanning chip calorimetry

FSC measurements were performed using a twin-type power-compensation Mettler-Toledo fast scanning chip calorimeter Flash DSC 1. It consists of two separated silicon nitride/oxide membranes with an area of 1.7 mm \times 1.7 mm and a thickness of 2.1 μm each, serving as sample and reference calorimeters. The membranes are surrounded by a silicon frame of 300 μm thickness, and a ceramic support. The circular measurement area with a diameter of 500 μm in the center of each membrane is coated with 0.5 μm aluminum and contains heaters and temperature sensors. Fig. 1 shows the samples of PA 6 (left) and iPP (right) investigated in the present work, as placed on the heatable area of the sample calorimeter. The thickness of the samples is about 20 μm and the lateral dimension is 100–200 μm . Subsequent the crystallization experiment in the Flash DSC 1, the sensor was removed from the main instrument and placed into an *x–y* sample stage such that the incident X-ray beam is oriented perpendicular to the membrane surface, passing through the sample. Further details about the particular FSC used, including schematics of the sensor, performance, calibration, and sample preparation are provided elsewhere [28]. In the present study, the FSC sensor was conditioned and temperature-corrected according to the specification of the instrument provider. Worthwhile noting, though systematic investigations have not been performed yet, that repeated exposure of the FSC sensor to intense X-ray radiation led to a loss of its functionality.

3. Results and discussion

Fig. 2 shows apparent heat capacity data of iPP as a function of temperature, calculated from heat-flow-rate data recorded on cooling the relaxed melt at different rate between 20 K s^{-1} (top curve) and 500 K s^{-1} (bottom curve). The data of Fig. 2 show two separate ordering processes at different temperatures. The high-temperature peak (C) is due to crystallization/formation of monoclinic crystals (α crystal phase) and the low-temperature peak (M) is due to mesophase formation. Cooling the quiescent melt at rates lower than 50 K s^{-1} leads to crystallization only, while solidification at rates between 60 K s^{-1} and 200 K s^{-1} additionally allows mesophase formation at lower temperature. If the cooling rate exceeds 200 K s^{-1} then formation of monoclinic α crystals cannot be observed anymore, and presence of the low-temperature peak suggests exclusive formation of mesophase. Cooling faster than 300–500 K s^{-1} leads to complete vitrification of the super-cooled melt at the glass transition temperature. It is important to note that the assignment of the various exothermic peaks to formation of different polymorphs is based on WAXS analyses of samples prepared separately. Only in this work, we analyzed for the first

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