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Short Communication

Two processes of α-phase formation in polypropylene at high supercooling

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ABSTRACT

The non-isothermal and isothermal crystallization of different types of commercial polypropylenes (PP) are investigated by fast scanning calorimetry and wide-angle X-ray scattering. Typically, PP shows two different crystallization processes: below 55 °C the mesophase formation and at higher temperatures the α-phase formation. Here we report the first observation of an additional crystallization process in some PP-types. It is observed between 45 °C and 75 °C, and is understood as a consequence of an additional nucleation of α-phase crystals.

1. Introduction

Polypropylene (PP) is a semi-crystalline polymer which is able to organize into different polymorphic phases [1–4]. In short, the most stable monoclinic α-phase is usually formed at low and medium supercooling. The formation of the hexagonal β-phase requires special nucleating agents or mechanical shear stress. The orthorhombic γ-phase is formed at elevated pressure and high temperatures. At high supercooling a mesomorphic or conformationally disordered phase is formed [5–7].

The isothermal crystallization kinetics of PP at high and medium supercooling can be easily investigated using fast differential scanning calorimetry (FDSC) [8–13]. Typically, two crystallization regions are observed at high and low temperatures, above and below 60 °C, corresponding to the formation of the α-phase and so-called mesophase, respectively. In a fast cooling experiment these crystallizations phenomena are measured below 40 °C (mesophase formation) and above 80 °C (α-phase formation), respectively. The mesophase formation only occurs with cooling rates between about 50 K/s and 1000 K/s. Recently, we reported on an additional crystallization process in PP highly filled with calcium carbonate ($CaCO_3$) [14]. For isothermal crystallization conditions this process occurs between 45 °C and 85 °C. It was interpreted as a consequence of a different nucleation mechanism induced by the filler.

In this contribution we report on a comparative analysis of the crystallization behavior of various commercial available polypropylenes using FDSC. For the first time we have found unfilled polypropylene homopolymer types which also show a total of three crystallization processes. We have studied these crystallization processes using fast scanning DSC and wide-angle X-ray scattering (WAXS).

2. Experimental

2.1. Samples

Seven different commercial polypropylenes were investigated using FDSC. The analyzed materials are listed in Table 1. M_w and M_n are the weight average and number average molecular weight, respectively. MFR is the melt flow rate. The data are taken from the material supplier. For iPP12 the viscosity is too low for MFR determination. This material has a low molecular weight and bad mechanical property, it is rather a wax. The different iPP types (from Aldrich) are isotactic polypropylenes. PPB and PPN are commercial homo-polymers with unspecified tacticity.

Inorganic fillers can induce an additional crystallization process [14]. To exclude a potential filler influence on the crystallization behavior we analyzed all materials using thermogravimetry to

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Table 1
List of the samples. $t_{1,min}$ is the minimum peak time for the low temperature crystallization process (process I in Fig. 2). MFR was determined for 2.16 kg at 230 °C.

Short name	Supplier	Name	M_w [kg/mol]	M_w [kg/mol]	MFR [g/10 min]
iPP580	Aldrich	427853	580	166	0.50
iPP340	Aldrich	427861	340	97	4
iPP250	Aldrich	427888	250	67	12
iPP190	Aldrich	427896	190	50	35
iPP12	Aldrich	428116	12	5	–
PPB	Borealis	HF136MO	390	140	20
PPN	Basell	Novolen 1106H	462	85	2

Table 2
Measured properties of the sample: T_c and T_m are the peak temperatures during cooling and subsequent heating at 10 K/min measured with conventional DSC. $T_{m,2}$ is the second peak temperature in case of double peaks, ΔH_m is the melting enthalpy. $t_{1,min}$ is the minimum peak time for the low temperature crystallization process (process I in Fig. 2) measured by Flash DSC.

Short name	T_c [°C]	T_m [°C]	$T_{m,2}$ [°C]	ΔH_m [J/g]	$t_{1,min}$ [ms]
iPP580	104.2	163.5	–	96.6	65
iPP340	109.9	162.9	–	100.8	72
iPP250	119.3	163.6	–	112.0	47
iPP190	112.4	158.2	162.9	102.2	68
iPP12	109.7	147.1	156.5	99.5	84
PPB	111.2	160.7	–	113.5	58
PPN	118.1	163.1	–	110.4	50

determine the inorganic filler content. The samples were heated with 30 K/min to 800 °C. At 600 °C the reactive gas was switched from nitrogen to oxygen. For none of the materials inorganic additives were detected. Characteristic data of the crystallization and melting process (temperature of the crystallization peak T_c) measured with conventional DSC (DSC3+ from Mettler-Toledo) are listed in Table 2. Samples of 5 mg were cooled and subsequently heated at rates of 10 K/min. The melting peak of iPP190 and iPP12 is bimodal and the specific melting enthalpy of iPP250, PPB and PPN is about 10% higher as the other materials. The crystallization temperature of iPP250 and PPN is about 10 K higher compared to the others. This may indicate the presence of additives or heterogeneities in the samples which accelerate the crystallization process.

2.2. Fast DSC (FDSC)

The measurements were performed using a METTLER TOLEDO Flash DSC1 with UFS1 sensor. The performance of this instrument is discussed in Ref. [15]. The sample support temperature was set to −80 °C. The measurements were performed with 55 ml/min nitrogen flow. A typical sample size of 50 ng was selected. The maximum melt temperature of the measurements was selected to be 190 °C. In a pre-study, it was investigated whether this temperature is sufficiently high to prevent the influence of memory effects [14,16].

The crystallization behavior was measured during cooling at various cooling rates between 1 K/s and 4000 K/s. Isothermal crystallization measurements were performed after cooling at 4000 K/s from the melt to the crystallization temperature investigated.

For each sample a new sensor was used. To increase the temperature measurement accuracy an indium sample was placed on the reference after all sample measurements and the melting temperature was measured at 100 K/s and 1000 K/s. The deviation between the measured melting temperature and the literature values was always less than 1 K.

2.3. Wide-angle X-ray scattering (WAXS)

WAXS measurements were performed in transmission using a SAXSLAB Ganesha 300 XL SAXS system operated at near-vacuum conditions with a source-ray photon wavelength of 1.54 Å. Patterns were acquired with an acquisition time of 100 s by means of a Pilatus detector with 487 × 619 pixels of 172 μm × 172 μm, placed at approximately 100 mm from the sample surface. All scattering data were background corrected and integrated using the software package FIT2D (ESRF, France).

3. Results and discussion

3.1. Non-isothermal crystallization

The crystallization behavior of the PP samples was measured at different cooling rates. The cooling rate dependence of the crystallization peak temperatures was evaluated. Most materials show the typical behavior of polypropylene [8,10,17]: At low supercooling a single crystallization peak occurs. At cooling rates faster than 50 K/s a second peak appears at temperatures below 55 °C. At cooling rates faster than 1000 K/s the material does not crystallize. The high temperature crystallization peak is caused by the α-phase crystallization. The low temperature crystallization is identified as mesophase formation [8,10].

Selected Flash DSC cooling curves of four materials (iPP340, iPP250, PPB and PPN) are displayed in Fig. 1. For comparison, the curves are normalized by the measured melting enthalpy after cooling from the melt at 1 K/s. We use this property as a measure of the sample size. The displayed curves are measured during cooling at 100 K/s and 200 K/s. At these cooling rates iPP340 and PPB show the normal behavior of PP: A crystallization peak at about 80 °C and a second peak around 30 °C. The low temperature peak is very small for PPB at 100 K/s. The curves of iPP250 show always two crystallization events. The peaks are close together in the temperature range between 60 and 100 °C. PPN shows at cooling with 100 K/s only one crystallization peak. The behavior is different to the other investigated materials but similar to the reported β-phase nucleated iPP results [11]. At cooling with 200 K/s the crystallization peak shows a weak indication of a shoulder on the low temperature side. The PNN curves at 300 and 400 K/s show that this event is more pronounced at higher rates.

Fig. 2 shows the peak temperatures of the crystallization peaks as a function of the cooling rate. The high temperature peak is shown by filled symbols. The unfilled symbols indicate the low temperature peak. iPP580, iPP340 and PPB show the well-known behavior discussed above. iPP12 behaves similarly, however, the mesophase is already formed at cooling with 20 K/s and the α-phase