



## The effect of modality on linear low-density polyethylene crystallization behaviour at high and very high supercoolings

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**Abstract.** Isothermal crystallization rates of uni- and bimodal linear low density polyethylenes having similar average molar mass and branching content were analysed at various temperatures in a very high supercooling range by means of a novel method – chip nanocalorimetry. At a particular crystallization temperature within the lower range of temperatures the bimodal material crystallized slower than the unimodal one, whereas at moderate supercooling temperatures bimodal polyethylene materials have earlier been reported to crystallize faster. Comparison to a high and moderate range of supercoolings was also made using an in-house built hot stage polarized light microscopy system. The difference gives evidence of a different crystallization mechanism caused by modality, which can have a strong impact on the application properties of the material.

**Key words:** linear low-density polyethylene, crystallization rate, unimodal, bimodal, high supercooling, chip nanocalorimetry.

### INTRODUCTION

Linear low-density polyethylenes (LLDPE) are co-polymerization products of ethylene and  $\alpha$ -olefins, 1-butene in the case of this work. The use of Ziegler–Natta (ZN) type catalysts when synthesizing LLDPEs makes them heterogeneous both in intermolecular and intramolecular terms [1], i.e. compared to materials synthesized by single-site catalysts, the ZN materials have a broad ethylene sequence length (ESL) distribution with considerable quantities of long sequences [1,2,3]. If unimodal LLDPEs are traditionally produced by a single reactor–catalyst system then bimodal polymer materials can be produced, besides using dual catalyst systems in a single reactor [4], in two cascaded reactors at different reaction conditions and feeds [5], which is comparable to blending two polymers of a different structure, resulting in a broad molar mass distribution (MMD). Furthermore, combining two reactors makes it possible to steer the MMD separately in the higher and lower MM ranges – to incorporate more branches in the longer polymer chains (inverse comonomer distribution) [6,7]. The heterogeneous short chain branching distribution (SCBD)

across the width of the copolymer MMD is known to influence mechanical properties [8,9,10]. Due to tie molecules that connect the crystal lamellae, these polymers show outstanding combinations of properties (stiffness plus resistance against slow crack propagation, toughness) [7]. The cooling mode influences the mechanical and thermal properties of the material through turnout morphology. Bearing in mind the cooling rates at industrial processing, which are by far higher than these of conventional calorimetric experiments (many materials are used in the metastable crystal state formed during quenching [11]), it is of practical interest to study the crystallization behaviour – if and to what direction MMD and SCBD affect the crystallization rate – of ZN LLDPE materials at temperatures in the high and very high supercooling ranges.

### EXPERIMENTAL

#### Materials

Two commercially available ZN LLDPE materials produced by Borealis Polymers OY were investigated, one of them bimodal and the other unimodal. The two materials differ mainly in the polydispersity index

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**Table 1.** Main parameters of the materials studied

Material	MFR2, g/10 min	Mw, kg/mol	PDI	Density, kg/m <sup>3</sup>	Comonomer content, wt. %
Bimodal	2	168	24.5	923	7.5
Unimodal	1	131	4.1	919	7.5

(PDI). A difference in weight average molar mass also exists but is not supposed to affect the crystallization rate in this range of supercooling [12]. Both materials are copolymers of ethylene and 1-butene and have similar average comonomer content. The characteristics of the materials are presented in Table 1. MMDs of the materials were measured in Borealis Polymers OY by gel permeation chromatography (GPC) using 1,2,4-trichlorobenzene as a solvent at 140°C. The average comonomer content was also measured in Borealis Polymers OY by Fourier transform infrared spectroscopy (FTIR).

### Successive nucleation/annealing (SNA)

The SNA [13] experiments were conducted with a Perkin-Elmer Pyris Diamond DSC instrument equipped with an Intracooler III. Nitrogen purge (20 mL/min) was used during the measurements for preventing oxidation of the samples. The instrument was calibrated by indium and zinc for temperature at scanning rates applied during subsequent measurements and by sapphire for heat flow. Flat sample slices of a mass of  $3.00 \pm 0.05$  mg were closed into aluminium capsules of a few milligrams of weight to minimize thermal lag. The sample was first melted at 180°C for 5 min to erase previous thermal history and then cooled to 30°C. Cooling and heating rates were 10 K/min in this entire experiment. Next, the sample was heated to an annealing temperature and kept at this temperature for 5 min. Crystallization was achieved by subsequent cooling to 30°C. The heating–annealing–cooling cycle was repeated at successively lower temperatures (step 5°C) from 126 to 91°C. After the final annealing, the sample was cooled to 0°C and reheated to 180°C at the same rate for obtaining the SNA endotherm.

### Chip nanocalorimetry (CNC)

Crystallization behaviour of the materials was studied by means of CNC, a method first introduced by Minakov and Schick [14]. Due to very small sample and sensor dimensions and thus heat capacity, nanocalorimetry minimizes the thermal lag and allows for cooling rates up to  $10^5$  K/s and hence high supercoolings (ca 80 K for LLDPE). The calorimetric sensors used in this work were XEN-39272 by Xensor Integration (heated area  $100 \times 100$  μm, thermophile sensitivity 2 mV/K). The sensor chip was thermostatted in a unique furnace, consisting of a ceramic ring-shaped electrical

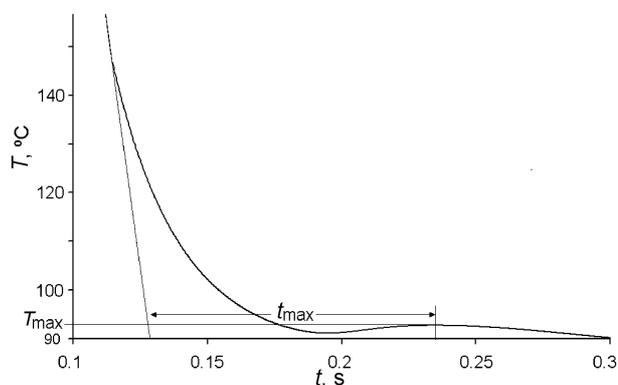
heater beneath the micro-sensor in a relatively massive (90 g) brass case with an inlet and outlet for nitrogen flushing.

To prepare the polymer samples, slices of 5 μm thickness were first cut by ultramicrotome (Ultratome 2128 by LKB), melted between two microscopy cover glasses, and pressed gently to reduce thickness. Using a razor blade or a surgical knife, samples of  $100 \times 100$  μm were cut under a preparation microscope to fit into the heated area of the sensor. When lifted onto the sensor chip, the sample was manually subjected to a short heating pulse of 3 V to melt it and make it adhere evenly to the sensor surface. The sensor chip with the sample was placed into the temperature controlled furnace. Prior to each series of calorimetric experiments the furnace was flushed with nitrogen in order to avoid oxidation of the sample.

Temperature of the furnace was measured with a resistance thermophile and controlled by means of an electronic temperature controller (TC200 Thorlabs) via a LabVIEW™ virtual instrument specially composed for this experiment.

An initial sharp pulse (2.3 V during 30 ms) was given to the film heater beneath the sample in order to melt the sample, then the heating voltage of the calorimetric chip was switched off to make the sample cool down as fast as possible to the constant furnace temperature. The temperature signal from the sensor was recorded at 6000 points per second. Every measurement lasted for 1 s.

Although the nanocalorimetric sensor enables cooling down the sample very fast, it still takes a finite time, so the starting moment of crystallization was counted not from the moment of turning the heating voltage off, but from the point where the steepest tangent to the cooling slope crosses the base line. Crystallization rate was estimated by the reciprocal of time to the local maximum of the temperature curve – the time moment when the exothermal effect of the crystallization process was the most intensive (Fig. 1).



**Fig. 1.** Graphical determination of the starting moment and rate of crystallization.

### Hot stage polarized light microscopy system (HS PLM)

An in-house built hot stage, mounted on a light microscope Axioskop 2 by Zeiss, was used to control and follow the crystallization process through optical changes. The device and the technique are similar to those described in [15]. The sample was first heated at 180 °C for 30 s in order to erase the thermal history and then cooled down to the chosen isothermal crystallization temperature at a rate of approximately 15 K/sec. When the temperature reached the isothermal level, image grabbing was turned on, 150 images were taken at equal intervals (3 to 25 frames per second), and the images were analysed subsequently. As crystals appear light between two polarizers with their principal planes crossed, the degree of crystallization at any particular moment was decided upon by the proportion of light pixels in the respective microscopy image. Crystallization rate was estimated by the reciprocal of time to the moment where the crystal growth was the fastest.

## RESULTS AND DISCUSSION

Information from size exclusion chromatography (SEC) (Fig. 2) illustrates the fact that the MMD of the bimodal material is broader. There is a significant difference in the low MM range, but the bimodal material contains also more high and ultra-high MM fractions. Still, the MM difference between the parent polymers of the bimodal material is not large enough to show two peaks in this cumulative curve. At the same time the SNA data (Fig. 3), revealing information about the SCBD, show that the bimodal material contains larger proportions of the longest and next but longest ethylene sequences, which crystallize during annealing at 126 and 121 °C, and less macromolecules of higher branching content, which crystallize during annealing below 121 °C.

Figure 4 illustrates the different crystallization behaviour of the ZN LLDPE materials resulting from the difference in the MMD and SCBD. Isothermal crystallization rate at very high supercoolings (below 100 °C) was measured by the CNC method, crystallization rate at high or moderate supercoolings (above 100 °C) was analysed by the unique HS PLM technique. A good correlation of the results obtained by different methods can be observed. The CNC and HS PLM results of the LLDPE materials fit into the same logarithmic extrapolation lines. The well-known fact that when moving downwards from the equilibrium melting temperature towards higher supercoolings, the isothermal crystallization rate increases with the degree of supercooling is proved also by the current study. From previous investigations it is known that materials with homogeneous structure (both MMD and SCBD),

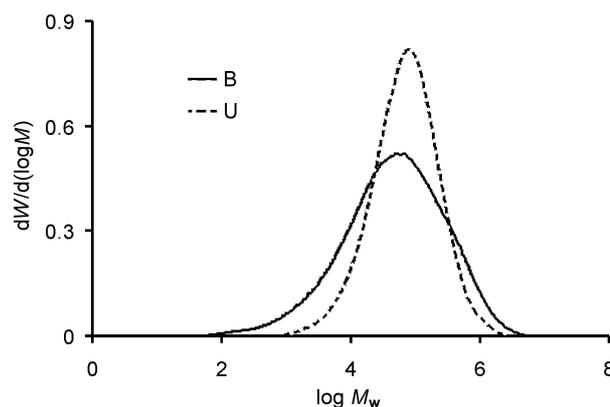


Fig. 2. Molar mass distributions of the materials by SEC. B – bimodal, U – unimodal.

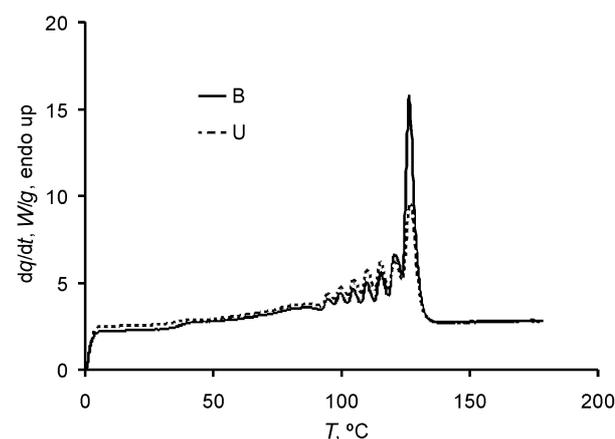


Fig. 3. Branching distributions of the materials by the SNA technique. B – bimodal, U – unimodal,  $q$  – heat flow.

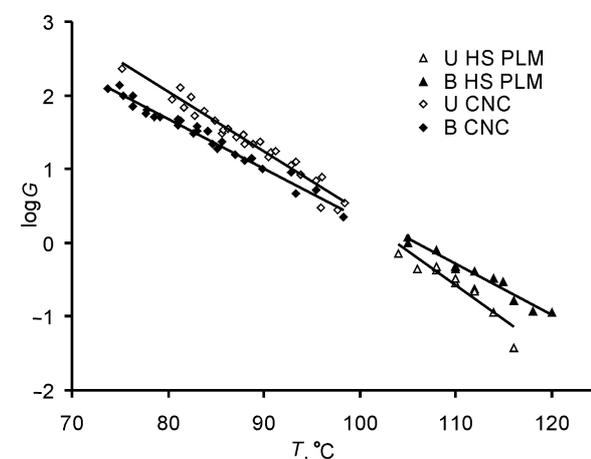


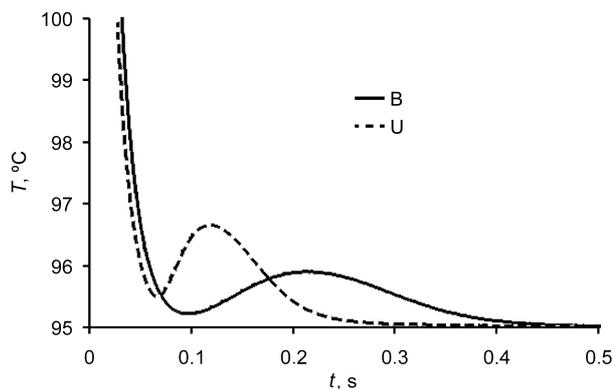
Fig. 4. Crystallization rate  $G$  of unimodal (U) and bimodal (B) LLDPE by CNC and HS PLM.

mainly produced by a single-site catalyst, crystallize slower than ZN materials having heterogeneous distributions and large proportion of long ethylene sequences at a similar average molar mass and branching content [1,3,12]. The current study also proves this phenomenon at temperatures above 100°C. However, at very high supercoolings the materials showed an unexpected behaviour. Below 100°C the unimodal material had a higher crystallization rate than the bimodal one. This is not in accordance with previous knowledge, as the bimodal material has certainly broader MMD and more long ethylene sequences by SNA than the unimodal one. The logarithmic extrapolation lines of the uni- and bimodal materials have a crossover point at approximately 100°C.

There have been several reports in the literature referring to disappearing differences in the crystal growth rate at higher supercoolings (or fast scanning rates) between materials of varied comonomer content, MM [12], or branch length (comonomer type) [16]. A recent study [9] compared a pair of bimodal blends of long and short HDPE macromolecules with matched MMD and average SCB (butyl) content, one blend having SCB preferentially incorporated on the longer chains, the other on the short ones. The mentioned study showed that at higher crystallization temperatures (i.e. lower supercoolings), placement of branches on longer molecules (analogous to the bimodal material in the current work) gives slower crystallization kinetics in comparison with the material with branches on the shorter molecules, and the difference diminishes towards higher supercoolings. These results are in agreement with the higher supercooling results of the current work.

It is generally understood that close to the equilibrium melting temperature methyl branches are incorporated into the crystal, giving rise to defects, hexyl and longer branches are mainly rejected from the crystal and ethyl branches have an intermediate behaviour, depending on the crystallization mode [16,17], or that ethyl branches are unconditionally rejected [3]. The diminishing difference and ultimate unification of crystallization rates towards higher supercoolings has been explained by a changed crystallization mechanism where branches are not excluded, somewhat similar to congealing [12].

The discovered phenomenon of intersection and opposite diverging of trends for the two otherwise similar materials differing only in heterogeneity (MMD and SCBD) further down the temperature scale could be explained by a lower final degree of crystallinity of the unimodal material, due to its lesser quantities of long linear sequences and faster crystallization rate. However, juxtaposition of crystallization peaks for the two materials measured at the same temperature (Fig. 5) does not confirm this suggestion (neither does rough calculation), as the areas of the peaks do not differ



**Fig. 5.** Comparison of crystallization behaviour of the unimodal (U) and the bimodal (B) materials at a furnace temperature of 95°C.

significantly. Examples are reported and discussed in the literature where under changing conditions one of several competing effects screens the others and becomes dominant. Under rapid cooling the effects of molar mass and branch content give way to that of sequence length distribution [12]. The molar mass effect gives way to that of branch content when the latter has become large enough [3,18]. Similarly, at sufficiently high supercoolings, where branches are incorporated into the crystals and behave like linear sequences, the effect of branching distribution appears to be overrun by the ultra-high molar mass constituent present in the bimodal material. Thus, the ultra-high molar mass constituent becomes a growing hindrance to crystallization due to entanglements. Other methods should be additionally applied to analyse with more precision the degree of crystallinity and turnout morphology, as crystallization mechanism must be reflected in the morphology.

## CONCLUSIONS

Chip nanocalorimetry is a method that makes possible crystallization studies at supercoolings that are close to industrial processing conditions. The relative crystallization behaviour of bimodal and unimodal LLDPE materials changes with the degree of supercooling – at very high supercoolings the unimodal material appears to crystallize faster than the bimodal one. The inverse trends of bimodal and unimodal LLDPE crystallization rates by CNC, compared to methods yielding more modest supercoolings, are indicative of a difference in the crystallization mechanisms, possibly related to the effect of the very high molar mass constituent, present in the bimodal material, which gradually becomes dominant as supercooling increases.

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## Modaalsuse mõju lineaarse madaltiheda polüetüleenil kristallisatsioonikäitumisele suuritel ja väga suuritel allajahutustel

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On analüüsitud kahe lähedase molaarmassi ja hargnemiste sisaldusega lineaarse madaltiheda polüetüleenil isothermilise kristallisatsiooni kiirusi erinevatel väga suuritel allajahutustel, kasutades uutset meetodit – kiipnanokalorimeetriat. Kõige madalamatel uuritud temperatuuridel kristallus bimodaalne materjal aeglasemalt kui unimodaalne samal temperatuuril, aga mõõdukate allajahutuste puhul on varasemast teada, et bimodaalne polüetüleen kristallub kiiremini. Suurte ja mõõdukate allajahutuste võrdlemiseks on uuritud samu materjale originaalse kuumaluse-polarisatsioonmikroskoopia seadme abil. Kristallisatsioonikiiruse suundumuste erinevus viitab modaalsusest tingitud erinevusele kristallisatsioonimehhanismis, millel võib olla tugev mõju materjalide kasutusomadustele.