



Behaviour of the very-low-temperature crystallization peak of linear low-density polyethylene

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Abstract. The crystallization behaviour of Ziegler–Natta (ZN) and single-site catalyst based ethylene–1-butene and ethylene–1-hexene copolymers with different comonomer content were studied by differential scanning calorimetry. In addition to a high-temperature crystallization peak, and for ZN copolymers in addition to a low-temperature crystallization peak, quite often a very-low-temperature crystallization peak (VLTCP) was observed at temperatures in between approximately 330 and 345 K. It was found that the VLTCP temperature decreased with increasing comonomer content and did not depend on the type of catalyst used. The fractional degree of crystallinity calculated from the VLTCP was independent of the chemical nature and content of the comonomers present as well as of the polydispersity of molar mass within the used range of magnitudes. However, crystallinity as related to the area of the VLTCP was strongly catalyst type dependent and was higher for the single-site catalyst used compared to the ZN catalyst used.

Key words: materials technology, linear low-density polyethylene, copolymers, low-temperature crystallization peak, differential scanning calorimetry.

INTRODUCTION

Polyethylene (PE) is available with a wide array of engineering properties to provide toughness, ease of processing, shrinkage rates, chemical abrasion, impact resistance, etc. The properties are largely determined by the characteristics of the polymer such as molar mass (MM), molar mass distribution (MMD), and degree of branching.

One method for providing the special properties is the copolymerization of ethylene and α -olefins, which has become increasingly important in the last two decades. These materials, collectively termed linear low-density polyethylene (LLDPE), have been synthesized using different types of catalysts and comonomers. Usually, 1-butene, 1-hexene, or 1-octene is used as the α -olefin comonomer. Random ethylene– α -olefin copolymers obtained by homogeneous single-site catalysts (SSC) show a homogeneous comonomer distribution (CD) and a narrow MMD [1], in contrast to traditional

Ziegler–Natta (ZN) catalysts, which lead to broad MMD and CD [2,3].

The crystallization in copolymers is markedly different from the crystallization of linear or slightly branched polymers, such as linear PE and high-density PE respectively [4]. In copolymers ethylene sequences of varying lengths (determined by branching frequency) are present abundantly. These sequences can only crystallize below certain temperatures, determined by their lengths. Therefore, a broad range of melting temperatures may be expected for the copolymers. The crystallization process in copolymers is further influenced by the fact that branches longer than methyl are predominantly excluded from the growing crystal [5]. However, it should be mentioned here that ethyl (1-butene as comonomer), being a ‘border case’ branch, is excluded from the crystal lattice at low cooling rates, and can be included at high cooling rates. The crystals formed under such conditions are much thinner and less perfect compared to those formed in the corresponding non-branched material.

Differential scanning calorimetry (DSC) has been the main technique used to study melting and crystal-

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lization behaviour. The results from the thermal analysis of heterogeneous, ZN ethylene- α -olefin copolymers [6–9] clearly indicate the existence of a triple crystallization mechanism in the ethylene copolymers: a sharp, high-temperature crystallization peak (HTCP), a broad low-temperature crystallization peak (LTCP) next to HTCP, and often a very-low-temperature crystallization peak (VLTCP) are observed. For SSC copolymers, and in general for homogeneous copolymers [7], just HTCP and, often, VLTCP are observed (see for an example [6, Ch. 9, fig. 9.11]).

One of the hypotheses of the origin of VLTCP is proposed in [10,11] for SSC-based LLDPEs. As it was mentioned above, the crystallization process in copolymers is predominantly governed by the length distribution of the crystallizable sequence. In a random copolymer, the frequent occurrence of branches along the polymer backbone fragments the chain into a number of shorter sequences. Taking this into account, Zhang et al. [10] and Mirabella [11] suggested that HTCP corresponds to the crystallization of ethylene with a large average sequence length (ASL) and VLTCP is related to the crystallization with a relatively short ASL.

Another point of view on the problem of VLTCP arises from the investigation of the homogeneous nucleation of PE. For this purpose in [12] low MM PEs were emulsified to separate the nucleation from the growth process and to remove macroscopic heterogeneous nucleation sites. Both a VLTCP and a HTCP were observed for the emulsified samples during DSC cooling scans. The degree of undercooling from the equilibrium melting temperature of linear PE (417 K) for the VLTCP was several tens of degrees (80–100 K) in contrast to non-emulsified samples, which had only a HTCP at a few degrees of undercooling. It was suggested that the HTCP in the cooling scans is due to heterogeneous nucleation of aggregated droplets and the VLTCP is related to the homogeneous nucleation of the un-aggregated emulsion droplets.

The same degree of undercooling (as mentioned above) was pointed out for single nanocrystals homogeneously grown from solution, consisting of a single crystalline lamella with a thickness of 6.3 nm covered by thin amorphous layers [13]. Therefore, it can be concluded that the VLTCP phenomenon can be caused by homogeneous nucleation as it has the same undercooling as pointed out above.

However, the origin of the VLTCP in ethylene-containing polymers is not clear yet. Therefore, the main aim of the present study was to examine the effect of the structure of materials, polydispersity of MM of the polymers, and comonomer type and its concentration on the behaviour of the VLTCP.

EXPERIMENTAL

Materials

The LLDPEs used in this study were commercial ethylene-1-butene and ethylene-1-hexene copolymers produced by ZN and SSC. The polymers will be referred to as ZN and SSC samples. The comonomer content, C_{comon} , in the copolymers varied. All these materials had similar density and weight average MM (\bar{M}_w). Molecular characteristics of the studied samples are listed in Table 1.

Methods

A Perkin Elmer Diamond differential scanning calorimeter (DSC) was used for thermal analysis. The instrument was calibrated using indium and tin at the applied cooling rate. Helium was used for furnace purge. Plates of $55 \times 65 \times 1$ mm were pressed from the materials at 453 K and cooled to room temperature. Flat samples of approximately 1 mg were cut from the plates and packed into aluminium foil to maximize thermal contact between the sample and the calorimetric furnace. During the measurement, the sample was first held at 453 K for 5 min for deleting its thermal history. Then it was cooled to 273 K at a rate of 100 K/min, held at 273 K for 5 min, and then heated to 453 K at a rate of 100 K/min. The fractional degree of crystallinity, w_c , was calculated by dividing the crystallization enthalpy of VLTCP by the enthalpy of the fusion of 100% crystalline PE, $\Delta H_m^0 = 293$ J/g. Crystallinity is, however, only to be used for comparison between the materials. The overall crystallinity ($w_{c,h}$) was obtained by dividing the overall melting enthalpy by 293 J/g.

The MMD was measured in Borealis Polymers OY by gel permeation chromatography (GPC) using trichlorobenzene as a solvent at 140 °C.

The comonomer content was measured in Borealis Polymers OY by Fourier transform infrared spectroscopy (FTIR).

Table 1. Molecular characteristics of linear low-density polyethylenes

LLDPE sample	Type of comonomer	C_{comon} , wt. %	Density, kg/m ³	M_w , kg/mol	Polydispersity M_w/M_n
SSC-1	1-Hexene	5.4	923	84	2.1
SSC-2	1-Hexene	3.6	927	140	3.1
SSC-3	1-Hexene	5.0	923	140	2.3
SSC-4	1-Hexene	6.9	920	115	2.4
SSC-5	1-Butene	2.3	922	136	2.3
ZN-1	1-Hexene	5.6	930	125	4.5
ZN-2	1-Hexene	7.6	924	125	4.4
ZN-3	1-Hexene	8.5	917	150	3.8
ZN-4	1-Butene	7.2	920	122	4.0

RESULTS AND DISCUSSION

The nonisothermal crystallization and melting thermograms for one of the materials (SSC-1) are shown in Fig. 1 as an example.

Figure 1 illustrates the presence of two distinct peaks in the crystallization curves of SSC-1 copolymer: a sharp HTCP and a much broader and less in magnitude VLTCP at temperatures around 340 K. Similar heating/cooling scans are observed for all the samples studied. In contrast, the melting of the materials has only one endothermic peak corresponding to their HTCP. It should be mentioned that for ZN as well as for SSC copolymers no clearly evident LTCPs were observed, except for sample ZN-3, where an additional small LTCP was clearly detected. Along with it an additional broad melting peak is present in DCS melting curves of this sample. For copolymers produced using ZN catalyst it was suggested [14] that HTCP is due to the crystallization of high MM polymers having a low branching content, whereas the LTCP and also VLTCP are caused by low MM polymers with a high branching content. However, the branching distribution is homogeneous in materials synthesized by SSC, without the clustering of the branch along the main chain as in ZN copolymers, and there should be no relation between MM and the branch content. However, the experimental results uniquely indicate that there was still a low-temperature crystallization process, leading to a VLTCP, as it is obvious from Fig. 1.

Figure 2 shows the dependence of the peak temperature of VLTCP, $T_{c,vi}$, on the comonomer content, C_{comon} , for ethylene–1-hexene copolymers. It is seen that as C_{comon} increases, $T_{c,vi}$ decreases, which is in agreement with the finding reported in [7]. An interesting fact is that $T_{c,vi}$ vs. C_{comon} for copolymers that have the same comonomer type can be represented by a single line, irrespective of the catalyst type by which

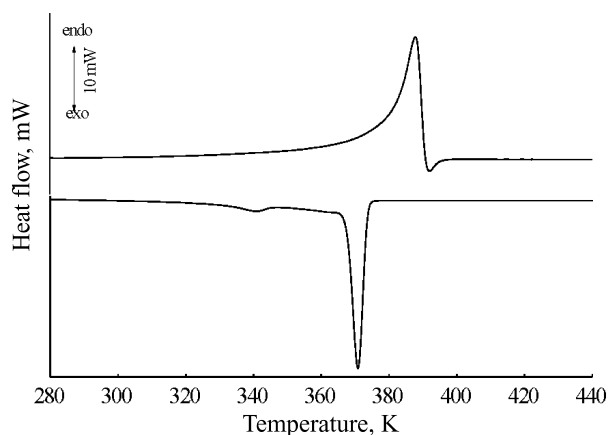


Fig. 1. DSC cooling and subsequent heating curves of sample SSC-1.

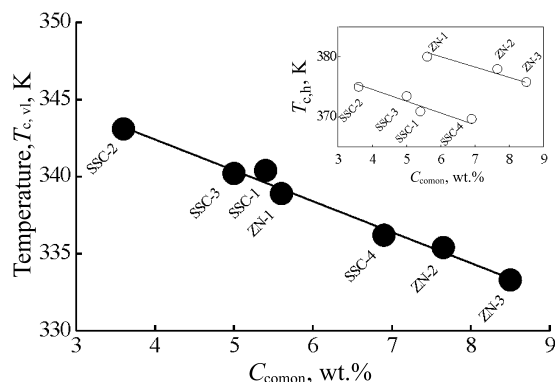


Fig. 2. Plots of peak crystallization temperatures of the VLTCP ($T_{c,vi}$) as a function of the comonomer content (C_{comon}) for the ethylene–1-hexene copolymers. The inset shows temperature dependence of the HTCP ($T_{c,h}$) on C_{comon} for the same copolymers.

the materials were produced. This differs from the behaviour of the HTCP. The temperatures of the main peak ($T_{c,h}$) for SSC materials were essentially lower than for ZN materials as is clearly seen from the inset in Fig. 2. The ZN copolymers are known to be structurally heterogeneous both at inter- and intramolecular level. Therefore, more and longer ethylene sequences are available leading to thicker lamellae and consequently to higher crystallization and melting temperatures according to the Thompson–Gibbs equation. Taking into account the above-mentioned difference in the behaviour of peak temperatures with catalyst type, one can suggest that it is not only the presence of long ethylene sequences that influences the thermal behaviour of VLTCP.

However, on further comparison between copolymers of different catalyst types, it was found that the type of catalyst, ZN and SSC, influences the crystallization process in the low-temperature range. These observations were further verified by comparing the fractional degree of crystallinity of VLTCP $w_{c,vi}$ vs. C_{comon} . Plots for all the copolymers are shown in Fig. 3. It was found that $w_{c,vi}$ did not depend either on the comonomer type and its content or on the polydispersity of MM within the same type of catalyst. The overall degree of crystallinity is known to be independent of the nature of the comonomer (except for methyl branches), while being largely determined by the crystallizable sequence length distributions [15,16]. In turn, the sequence distributions are influenced by the type of catalyst (e.g., ZN-based systems result in broader distributions compared to SSC-based copolymers).

The fractional degree of crystallinity calculated from VLTCP is two times higher for the SSC copolymers than for the ZN materials as is seen from Fig. 3. It is evident that homogeneous CD facilitates the formation of a VLTCP. However, thermal analysis alone is not sufficient for explaining this behaviour.

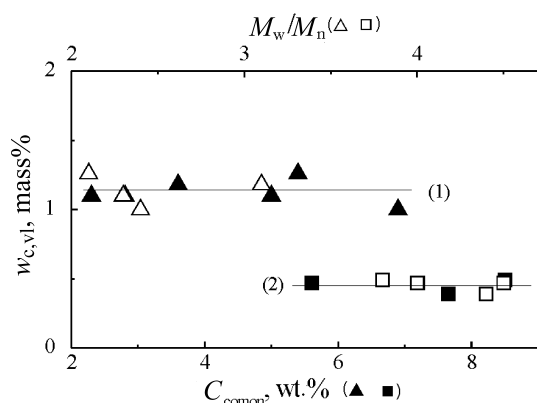


Fig. 3. The degree of crystallinity $w_{c,vi}$ vs. comonomer content C_{common} (solid signs, bottom of X-axis) and polydispersity M_w/M_n (open signs, top of X-axis) for SSC (1) and ZN (2) copolymers.

An interesting and important fact detected in calorimetric cooling and heating scans is that no low-temperature melting peaks corresponding to the VLTCF were found for the studied LLDPE materials. Hence, the origin and properties of the VLTCF cannot be explained only in terms of the crystallization of ethylene sequences having a relatively short ASL. In this case the lamellae population formed at low temperature should be thin [11] and therefore should melt at a considerably low temperature. This is not observed for the studied materials, which have essentially large VLTCFs at undercoolings ~ 80 K. The same degrees of undercoolings were detected in [12,13] for homogeneously grown crystals of PE. Probably, the VLTCF is associated with homogeneous nucleation, which occurs spontaneously by undercooling only.

CONCLUSIONS

On the basis of the DSC experimental results on the low-temperature crystallization behaviour of SSC- and ZN-based ethylene- α -olefin copolymers the following conclusions can be drawn:

- DSC curves uniquely indicate that in the studied copolymers an additional crystallization process occurred at very low temperatures around 330–345 K. This VLTCF is much broader and less in magnitude than the main sharp HTCP. Moreover, the melting curves do not show any additional peaks clearly related to the VLTCF.
- No dependences of the fractional degree of crystallinity calculated from the VLTCF on the comonomer content and polydispersity of MM were observed at least within the studied range of magnitudes. The degree of crystallinity was also independent of the chemical nature of the comonomers (1-butene or 1-hexene).

- The fractional degree of crystallinity was in turn strongly influenced by the type of catalyst. For the SSC materials the degree of crystallinity was higher than for the ZN samples.
- The crystallization temperatures of the VLTCF, $T_{c,vi}$, decreased with the increasing comonomer content in the LLDPEs. At the same time, $T_{c,vi}$ did not depend on the catalyst type used for producing the LLDPE materials.

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Lineaarse madaltiheda polüetüleenini väga madala temperatuuri kristallisatsiooni piigi olemus

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Diferentsiaalse skaneeriva kalorimeetriaga on uuritud Ziegleri-Natta (ZN) ja ainuasendi (SSC) katalüsaatoritega saadud erineva komonomeeri sisaldusega etüleen/1-buteen- ning etüleen/1-hekseenkopolümeeride kristallisatsioonikäitumist. Lisaks kõrge temperatuuri kristallisatsiooni piigile (KTKP) ja ZN-i kopolümeeride puhul lisaks madala temperatuuri kristallisatsiooni piigile (MTKP) on tuvastatud tihti ka väga madala temperatuuri kristallisatsiooni piik (VMTKP) temperatuurivahemikus ligikaudu 330–345 K. On leitud, et VMTKP maksimumi temperatuur väheneb koos komonomeeri sisalduse kasvuga kopolümeeris ja ei sõltu kasutatud katalüsaatori liigist. VMTKP põhjal arvatud kristalsusmäär ei sõltu uuritud materjalide puhul komonomeeri keemilisest koostisest (1-buteen või 1-hekseen), komonomeeri sisaldusest ega molaarmassilise jaotuse polüdisperssusest. Siiski sõltub VMTKP kristalsusmäär tugevalt kopolümeeride valmistamiseks kasutatud katalüsaatori liigist ja on kõrgem SSC katalüsaatori puhul, võrreldes ZN-i katalüsaatoriga.