Study of Very Low Temperature Crystallization Process in Ethylene/α-Olefin Copolymers

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Summary: The crystallization behavior of Ziegler-Natta (ZN) and single site (SS) based ethylene/1-butene and ethylene/1-hexene copolymers and SS copolymer fractionated by composition and molar mass (MM) has been studied by differential scanning calorimetry. It was observed that in addition to the high temperature crystallization peak (HTCP), and for ZN copolymers in addition also to low temperature crystallization peak (LTCP), a very-low temperature crystallization peak (VLTCP) is present at temperatures in between 60–75 °C. Peak temperature of VLTCP, T_{VLTCP}, decreases with increasing comonomer content (C_{comon}) at fixed MM. If C_{comon} is kept approximately constant, T_{VLTCP} increases with increasing MM. It turns out that T_{VLTCP} does not depend on the type of catalyst used. The degree of crystallinity calculated from the VLTCP is independent of the chemical nature of the comonomers present, but slightly changes with C_{comon}. It also steeply increases with MM and levels off at MM around 50 kg/mol. It was found that the crystallinity as related to the area of the VLTCP is catalyst type dependent, and is higher for the SS catalyst used compared to the ZN catalyst.

Keywords: crystallization at very low temperature; differential scanning calorimetry; ethylene/α-olefins; linear low-density polyethylene

Introduction

The crystallization of copolymers is markedly different from the crystallization of linear or slightly branched polymers, such as linear polyethylene and high-density polyethylene, respectively.[1] 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 the methyl are predominantly excluded from the growing crystal.[2]

Differential scanning calorimetry (DSC) has been one of the main techniques used to study melting and crystallization behavior of polymers. The results from the thermal analysis study on heterogeneous, Ziegler-Natta (ZN) ethylene/α-olefin copolymers[3–6] 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). For single site catalyzed (SS) copolymers, and in general homogeneous copolymers,[4] the high temperature crystallization peak and the very-low temperature crystallization peak are usually detected.

The presence and behavior of VLTCP in copolymers is interesting, because there is a possibility of correlation between this secondary crystallization process and the mechanical properties of the samples. One of the hypotheses of the origin of VLTCP is

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proposed in Ref. [7–9] for SS based linear low-density polyethylenes (LLDPE). As it was mentioned above, the crystallization process in copolymers is predominantly governed by the crystallizable sequence length distribution. In a random copolymer, the frequent occurrence of branches along the polymer backbone fragments the chain into a number of shorter sequences. While the longest sequences form part of the lamellar crystals, they impose a constraint on the remaining crystallizable sequences in these chains. As the number of segments participating in lamellar formation increases, so do the restrictions imposed on the mobility of the remaining sequences. At very high degrees of constraint, the shorter sequences are unable to participate in the reeling-in process required for chain-folded crystal formation. The easiest route available for this short segments to crystallize without violating spatial requirements is to simply aggregate into thin bundles.[9] Accordingly, they aggregate with neighboring sequences to form stable clusters or bundled crystals. It is also suggested that the bundled crystals may act as cross-linking points in the amorphous phase. H. Teng et al.[10] stated by means of atomic force microscopy that there is a clear regular structure between spherulites and a lot of bundle-like bridges spanning the neighboring spherulites in bulk-crystallized polyethylene (PE). With increasing the branch component in the blend of linear and branched PEs the regular structure between spherulites disappeared.

However, the origin of the VLTCP in ethylene-containing polymers is not clear up to now. It is well known that many properties of crystalline random copolymers are very dependent on molar mass (MM) and crystallization conditions.[11–13] Consequently, to get appropriate properties of copolymers, along with the sequence distribution (SD) and concentration of comonomer (C_{comon}) the MM and crystallization condition have to be specified and independently assessed. Therefore, the major focus of the present study is to examine the effect of structure of materials, co-monomer type and its content, MM and different cooling/heating rates on the behavior of the VLTCP. Moreover, one of the SS catalyzed copolymer was fractionated by MM and composition to analyze the contribution of MM and C_{comon} as independent variables.

Experimental Part

Materials

The LLDPE's used in this study were commercial ethylene/1-butene and ethylene/1-hexene whole copolymers, produced by ZN[14] or SS[15] catalyst types. The molecular characteristics of the investigated ethylene copolymers are listed in Table 1. The samples are identified with the initials SS or ZN followed by a number corresponding to the comonomer content, C_{comon}, expressed in weight percent. All these materials (obtained in pellet form) had about the same density and weight average MM ($\overline{M}_{\mathrm{w}}$). One of the SS materials, namely SS-6.9, was fractionated according to both MM and composition. All the fractionations were carried out on polymer in powder form. For this purpose, the sample pellets were dissolved in xylene. The solution obtained was allowed to cool to room temperature and the polymer was precipitated in acetone, filtered and dried at room temperature. Fractionation by MM was carried out according to the Holtrup technique which is a solvent/non-solvent extraction.[16] In the experiment 10 g of polymer powder was extracted in a solvent/non-solvent mixture of xylene and ethylene glycol monoethyl ether in different ratios at 116 °C. Dissolution time of 10 min was used at each dissolution step, and 10 fractions were collected. Fractionation according to short chain branching (composition) was carried out using multiple solvent extraction[17] technique. The sample amount fractionated was about 15 g and dissolution time was 30 min. The solvents used in the fractionation were: n-pentane at 35 °C, n-hexane at 65 °C, n-heptane at 75 °C and 90 °C, n-octane at 100 °C, toluene at 105 °C

Table 1.
Molecular characteristics of single site (SS) and Ziegler-Natta (ZN) catalyzed copolymers.

		Sample	Comonomer type	C_{comon}	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
				(wt%)	(kg/mol)	arbitrary units
Whole polymers		ZN-5.6	hexene	5.6	125	4.5
		ZN-7.2	butene	7.2	122	4.0
		ZN-7.6	hexene	7.6	125	4.4
		ZN-8.5	hexene	8.5	150	3.8
		SS-2.3	butene	2.3	136	2.3
		SS-3.6	hexene	3.6	140	3.1
		SS-5.0	hexene	5.0	140	2.3
		SS-5.4	hexene	5.4	84	2.1
		SS-6.9 (6.2)	hexene	6.9 (6.2)	115	2.4
Fractions of SS-6.9(6.2) by	molar mass	M1	hexene	NA	5.1	2.1
		M2	hexene	NA	13.6	1.6
		M3	hexene	NA	20.1	1.6
		M4	hexene	NA	25.4	1.5
		M5	hexene	5.6	35.0	1.4
		M6	hexene	5.8	43.4	1.5
		M7	hexene	6.3	66.5	1.5
		M8	hexene	6.2	82.4	1.6
		M9	hexene	6.2	128	1.8
		M10	hexene	6.4	117	1.8
	composition	C1	hexene	6.5	98.5	2.5
		C2	hexene	5.9	100	2.3
		C3	hexene	5.4	96	2.2
		C4	hexene	3.9	99.5	2.1

'NA' means 'not analyzed'; M1, M2,. . .C1,C2 . . . are the numbers of fractions.

and xylene at 130 °C. The first two fractions were separated by evaporation of the solvent in a rotavapor and the other ones by precipitation in acetone. Due to the reasonably narrow composition distribution of sample SS-6.9, the first three compositional fractions were too small for further analyses. For comparison with LLDPE fractions the commercial Ziegler-Natta catalysed high-density polyethylene (HDPE) with $M_w = 94500$ and polydispersity $\overline{M}_w/\overline{M}_n = 8.3$ was fractionated according to MM. The fractions of HDPE have approximately similar polydispersity equal 1.7 in average.

As it follows from the fractionation description the whole SS-6.9 was dissolved, dried and obtained in powder form. Probably, due to the dissimilarity in material form (pellet or powder) there was a difference in melting and crystallization temperatures as well as in the degree of crystallinity of SS-6.9. Moreover, the value of C_{comon} for powder SS-6.9 was estimated to be about 6.2 wt%. The difference in C_{comon} may be connected with the different material forms (determination of C_{comon} was calibrated with pelletized samples). Therefore, this material was identified as SS-6.9(6.2). For comparison with the fractions the fluffy SS-6.9(6.2) powder was chosen as the reference material. The MM fractions have similar polydispersity $\overline{M}_w/\overline{M}_n$ and approximately identical C_{comon}. The C_{comon} for the first four fractions was not analyzed due to their small amount. The compositional fractions used in this work have about the same molar mass distribution and $\overline{M}_w$.

Methods

Perkin Elmer Diamond differential scanning calorimeter (DSC) and DSC-7 were used for thermal analysis at scanning rates of 10, 100, 300 °C/min and 5 °C/min, respectively. The instruments were calibrated using indium and tin at all applied heating rates. In Diamond DSC helium was used as furnace purge gas and in DSC-7 nitrogen was used. $55 \times 65 \times 1$ mm plates were pressed from the materials in pellet form at 180 °C and cooled to room temperature. For fractions powders were manually compacted by pressure at room temperature. To avoid differences in melting and crystallization temperatures caused by variation in sample weight, a sample mass of 1.00 ± 0.02 mg was used in all DSC experiments. Flat samples were packed into aluminum foil to maximize thermal contact between sample and calorimetric furnace. During the measurement, the sample was first held at 180 °C for 5 min for deleting its thermal history. Then it was cooled to 0 °C at a definite scanning rate, held at this temperature for 5 min and then heated to 180 °C at the same rate. Overall degree of crystallinity X_{overall} was calculated by dividing overall melting or crystallization enthalpy by enthalpy of fusion of 100% crystalline PE, $\Delta H_m^o = 293$ J/g. The partial degree of crystallinity estimated from the area of VLTCP, X_{VLTCP}, was obtained from cooling traces by dividing the crystallization enthalpy of VLTCP by ΔH_m^o.

MM averages and MMD were determined by size exclusion chromatography (SEC) using 1,2,4-trichlorobenzene (TCB) as eluent at 140 °C. Comonomer contents were measured by Fourier transform infrared spectroscopy (FTIR).[18]

Results and Discussion

The nonisothermal crystallization and melting thermograms for all SS and ZN whole materials were studied. Several selected exotherms of copolymers with different branch content at the constant cooling rate of 100 °C/min are shown in Figure 1. The similar heating/cooling thermograms are observed for all the samples studied at all scanning rates used.

Figure 1 illustrates 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) close to HTCP, and a very-low temperature crystallization peak (VLTCP), extending to temperatures around 60–75 °C, are observed. For SS copolymers studied, just the HTCP and VLTCP are usually observed. It should be noticed here that for whole HDPE no VLTCP and even LTCP were observed.

Nevertheless, the melting curves of the LLDPE materials have only one or seldom two endothermic peaks corresponding to primary crystallization presented by HTCP and LTCP. No additional peaks clearly related to the VLTCP were detected for none heating rate, as it is obvious from the Inset of the Figure 1. Due to this fact no melting temperature directly corresponding to the VLTCP (and also, partial crystallinity) can be obtained from the melting traces. We suggest that the crystallization temperature of the copolymer will

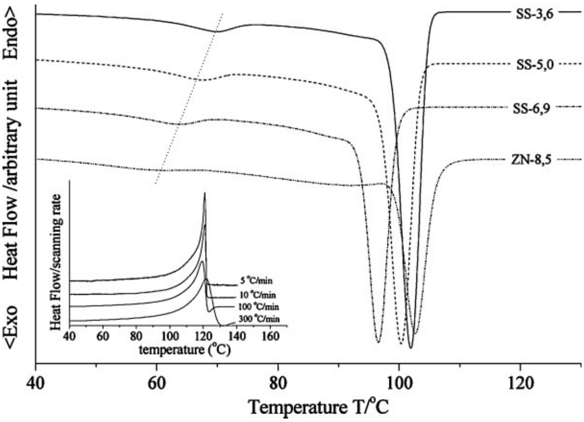

Figure 1.

DSC exotherms of ethylene-hexene copolymers measured at cooling rate of 100 °C/min. Inset shows DSC endotherms divided by scanning rates of SS-3.6 copolymer at different scanning rates.

accordingly behave itself with the melting temperature and such parameters as C_{comon}, MM, scanning rate etc. affects the melting and crystallization temperatures in a consistent manner. Therefore, in this work just the high and the very low temperature crystallization peaks, their crystallinity and temperatures, are mainly discussed. The temperatures used are the peak temperatures.

For copolymers produced using ZN catalyst it was suggested[19] that the HTCP is due to the crystallization of high MM polymers having low branching content, whereas the LTCP is caused by low MM polymers with high branching content. The VLTCP was also referred to the highly branched low MM chains.[7–9] However, the branching distribution is homogeneous in materials synthesized by SS catalysis, without the localization of branch along the main chain as in ZN copolymers, and there should be no relation between MM and branch content. However, the experimental results uniquely indicate that there is still a low temperature crystallization process, leading to a VLTCP, as it is obvious from Figure 1. From this figure it is also clearly seen there is some dependence of T_{VLTCP} on C_{comon} of the copolymers.

Indeed, Figure 2 shows the dependence of T_{VLTCP} on scanning rate for several selected samples with different C_{comon} produced by ZN and SS type of catalyst. The temperature corresponding to the main sharp crystallization peak (T_{HTCP}) is rate-dependent, shifting to lower temperatures at higher cooling rates. The VLTCP also depends on scanning rate, as it is evident from the Figure 2: the higher the cooling rate the lower is the T_{VLTCP}.

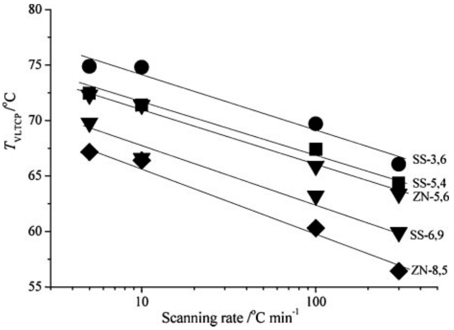

Figure 2.
Dependence of temperature of the VLTCP, T_{VLTCP} on scanning rate for selected SS and ZN based copolymers.

This figure also shows the dependence of T_{VLTCP} on C_{comon} of copolymers studied. It is seen, as C_{comon} increases, T_{VLTCP} decreases for all scanning rates in agreement of the finding reported in works.[4,32] A decrease in T_{VLTCP} (and consequently in crystallite size) is expected with increasing the number of branches in a given chain due to the decreased number of crystallizable units. In our previous work[20] we detected that for 100 °C/min scanning rate the T_{VLTCP} *vs.* C_{comon} for copolymers, having the same comonomer type, can be represented by a single line, irrespective of the catalyst type by which the materials were produced. The same behavior is observed in present study for all used scanning rates. Taking into account similar MM of the used materials (see Table 1), the conclusion can be reached that SS and ZN copolymers possess approximately the same thickness of crystallites associated with the VLTCP. Such behavior differs from that of HTCP. The temperatures of the main peak (T_{HTCP}) for SS materials are essentially lower than for ZN materials if C_{comon} is fixed, due to the structural heterogeneity of ZN copolymers both in inter- and intramolecular level.[20] Therefore, more and longer ethylene sequences are available in ZN materials leading to thicker lamellae and consequently to higher crystallization and melting temperatures according to the Thompson-Gibbs equation. Considering above mentioned difference in behavior of peak temperatures of HTCP and VLTCP with catalyst type, one can suggest that not only the presence of long/short ethylene sequences plays the role in thermal behavior of VLTCP.

An important element of phase structure is the degree of crystallinity. It should be noted here, that the partial degree of crystallinity calculated from VLTCP, X_{VLTCP}, displays scanning rate dependence.

Crystallinity value decreases with increasing scanning rate, and appear to reach a nearly constant value when scanning rate is higher than 100 °C/min. It is well known that at low scanning rate there is enough time for chains to be incorporated into the crystal lattice and more perfect and larger crystals are formed in comparison to those obtained at high cooling rate.

On further comparison between copolymers of different catalyst types, the interesting and unusual effect was found. For ZN materials the shape of the VLTCP is broader and less in magnitude than for SS materials having approximately the same comonomer content C_{comon} (see Figure 1). However, their peak crystallization temperatures T_{VLTCP} are similar. As is seen from the Figure 3 where the plots of X_{VLTCP} *vs.* T_{VLTCP} for all the copolymers are presented, in spite of identical T_{VLTCP}, X_{VLTCP} is approximately two times higher for the SS copolymers compared to the ZN materials.

This figure also shows that X_{VLTCP} does not depend on T_{VLTCP} and comonomer type within the same type of catalyst. It should be noted that MM for all whole copolymers was approximately similar (see Table 1) and higher than 80 kg/mol. As it will be shown below for fractionated SS-6.9(6.2), X_{VLTCP} does not change with T_{VLTCP} if MM is higher than 40–50 kg/mol. The independence of crystallinity on nature of the comonomer (except for methyl branches) is well known for the HTCP, because the degree of crystallinity mostly determined by the crystallizable sequence length distributions.[21,22] In its turn, the sequence distributions are influenced by the type of catalyst (e.g., ZN based systems result in broader distributions compared to SS based copolymers). It is evident, that homogeneous CD facilitates formation of the VLTCP. However, thermal analysis alone is not sufficient for explaining this behavior.

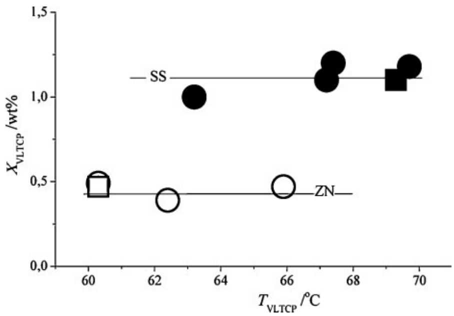

Figure 3.
Plots of VLTCP fractional crystallinity X_{VLTCP} *vs.* peak temperatures of VLTCP, T_{VLTCP}, for all used SS and ZN based ethylene/1-butene (squares) and ethylene/1-hexene (circles) copolymers. Scanning rate is 100 °C/min.

In Figure 4 the X_{VLTCP} is plotted as a function of C_{comon} for whole copolymers at two selected scanning rates. Data for compositional fractions of SS-6.9(6.2) are also presented in the Inset to the figure. It is evident that the introduction of the non-crystallizing co-units into the chain does not influence the level of X_{VLTCP} for whole copolymers. There is only slight tendency to decrease when C_{comon} is higher than 6 wt%. For compositional fractions having the same MM the decrease in X_{VLTCP} at C_{comon}>6 wt% is a little bit steeper. It should be noted that the degree of crystallinity that is attained in an actual crystallization process is not a measure of the minimum or maximum sequence that

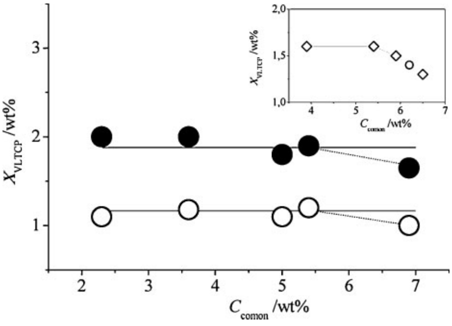

Figure 4.
Plots of VLTCP fractional crystallinity X_{VLTCP} *vs.* C_{comon} for all SS copolymers at 5 °C/min (solid circles) and 100 °C/min (open circles). The inset shows the plots X_{VLTCP} *vs.* C_{comon} for SS-6.9(6.2) fractions obtained by fractionation according to structure. The open circle in the Inset represents the whole unfractionated SS-6.9(6.2) copolymer at 100 °C/min.

participates in the crystallization, which is directly related to C_{comon}. Rather it is the sum over all possibilities, which can lead to independence of crystallinity with C_{comon} up to definite value.

Many properties of crystalline polymers are dependent on chain length.[11,13,23,24] The phase structure that defines the crystalline state can be varied by changing the MM and/or crystallization conditions.[13,25,26] Since random copolymers would be expected to behave in a similar manner, the influence of MM as an independent variable has to be investigated. The best way for studying the influence of MM on copolymer structure and properties is the fractionation of copolymer. However, for fractions of ZN copolymer the less branched fractions have the highest MM, and consequently, possible role of MM in influencing the thermal behavior and other structural properties are hard to recognize.

A definite influence of the MM on temperature and degree of crystallinity can be observed for SS based LLDPE fractions. For this purpose the whole copolymer SS-6.9(6.2) was fractionated by both MM and composition. Molar mass fractions have approximately constant branching content 6.2 ± 0.4 wt%. Compositional fractions have the same MM = 100 ± 2 kg/mol and different comonomer content (see inset in Figure 4).

For all molar mass fractions, except the first one with MM = 5.1 kg/mol, and all compositional fractions two (seldomly three) crystallization peaks in cooling thermograms were observed – HTCP and VLTCP (and seldomly LTCP). The first fraction does not display the VLTCP at all.

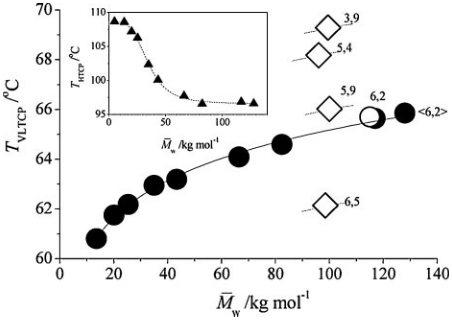

Figure 5.
Plot of peak temperatures T_{VLTCP} against $\overline{M}_{\mathrm{w}}$ for MM (solid circles) and compositional (open rhombs) fractions of SS-6.9(6.2). The point for unfractionated, whole, copolymer is also included and marked as an open circle. The data labels represent the values of C_{comon}. Inset shows the dependence of peak temperatures of the main crystallization peak T_{HTCP} vs. M_{w} for MM fractions of SS-6.9(6.2). Cooling rates are 100 °C/min.

As has been stated in Ref. [11], the influence of MM on the crystallization/melting temperature of the HTCP is not specific to a given copolymer type but is a general phenomenon for all types of branches. It was observed that the influence of MM is much more marked for the copolymers, than for linear PE, especially in the range of MM between 5 and 100 kg/mol.[11,12] For our samples the T_{HTCP} (and also melting temperature T_{m}) levels off above a molar mass of about 50–70 kg/mol as is seen from the inset to the Figure 5. R. Alamo et al. suggested[29,30] for fractions of ethylene/α-olefin copolymers having constant branch content that the reduction of the T_{HTCP} (as well as T_{m}) with increasing MM is a consequence of the decreased crystallite thickness of dominant lamellae. An explanation for the formation of smaller crystals with increasing MM is related to the slower crystallization kinetics due to the increase in entanglements. It has been demonstrated that not only crystallite thickness but also the nature of lamellae formed are affected by MM.[11] The lamellae that were long and straight at MM of 7 kg/mol have been observed to become short and highly segmented for MM of 70 kg/mol. The lateral dimensions of the lamellae are also decrease with MM.

The VLTCP behaves in absolutely opposite manner than HTCP does. As it is seen from Figure 5, while the T_{HTCP} decreases, the T_{VLTCP} grows with the increasing MM. T_{VLTCP} steeply increases in the range of MM $5 \div 70$ kg/mol, and tends to level off at $M_{\mathrm{w}} > 70$ kg/mol.

The data for compositional fractions of SS-6.9(6.2) is also drawn in Figure 5. These plots indicate that the less branched copolymers display the higher values of T_{VLTCP}. It is in agreement with the data for whole copolymers shown in Figures 1 and 2. Probably, the data for compositional fractions will generate a family of curves in plots $T_{VLTCP}(M_w)$, each dependent on C_{comon} and having the functional form as presented for $C_{comon} = 6.2$ wt% (drawn with solid line in Figure 5).

Since we have studied the influence of MM as an independent variable on the crystallization temperature of the VLTCP, we examined next its influence on the degree of crystallinity. Figure 6 represents the dependences of the degrees of overall ($X_{overall}$) and partial VLTCP (X_{VLTCP}) crystallinities of MM fractions of LLDPE SS-6.9(6.2) on M_w. For comparison in the given figure the data for MM fractions of HDPE are also included.

The decrease in the overall crystallinity of the fractions with MM agrees with that observed in works[13,29,30] for copolymer and linear polymer fractions. As it was supposed[11,29,30], increasing MM increases the density of chain entanglements in the melt. It gives us the opportunity to suggest that increasing chain entanglements reduce the ability of chains to participate in the primary crystallization process at high temperature and to form large dominant crystallites. It results in a significant increase of the amorphous layer thickness.[33] This means that the proportion of non-crystallized chains in the amorphous regions, which further can participate in the secondary crystallization at lower crystallization temperature, increases. As it is evident from the Figure 6, in the range of MM from 5 up to 40–50 kg/mol X_{VLTCP} sharply increases. At MM > 40–50 kg/mol the degree of crystallinity X_{VLTCP} does not change any more. It seems that the crystallinity of the VLTCP depends on whether the fraction of crystallizable sections of polymer macromolecules is incorporated into the main peak. Less incorporation will cause that VLTCP to grow in size or/and amount and reach some kind of equilibrium with dominant crystallites at critical MM ≈ 40–50 kg/mol. The most probable the value of critical MM is not a universal parameter and can differ with C_{comon}, polydispersity of MM, etc.

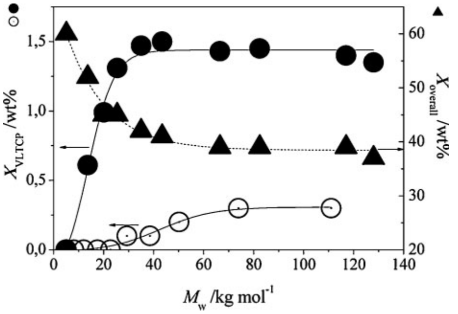

Figure 6.
Dependence of VLTCP crystallinity X_{VLTCP} (circles; left Y-axis) and overall crystallinity $X_{overall}$ (triangles; right Y-axis) on M_w of SS-6.9(6.2) fractions (solid circles and triangles) and HDPE fractions (open circles), which were obtained by fractionation of whole polymers by molar mass. Cooling rate used is 100 °C/min.

Because there is some clear correlation of HTCP and VLTCP with MM, it can imply that these exotherms are consequences of melt topology defined by entanglements. However, not only the melt topology, but also the presence of the branch defines the existence and properties of VLTCP. Indeed, as it is clear seen from the comparison of the curves for LLDPE and HDPE fractions in Figure 6, for branched polymer the crystallinity of VLTCP, X_{VLTCP}, is in around 5 times higher than for approximately linear polymer (having a few branches).

An identical behavior as presented in Figure 6 for VLTCP is observed for the dependence of X_{VLTCP} on T_{VLTCP}.

On this stage of our investigation it is hard to suggest the morphology structure of VLTCP crystallites. According to the model for copolymer crystallization proposed in *Introduction* section, two distinct modes of crystallization can be a result of two vastly different morphologies operated in the copolymers – lamellae and bundled crystals.[8,9] Following this model the HTCP can be attributed to crystallization of polymer chains having high MM and low branching content, while VLTCP is comprised of the less crystallizable, lower MM, more highly branched chains.[7] If there was the case, for ZN fractions the polymer molecules associated with the VLTCP would be eluted first in the temperature rising elution fractionation (TREF) process. Hence, fractions with higher MM would be expected to exhibit only the HTCP. However, as it was shown in work,[32] all the MM fractions of ZN copolymer, obtained by preparative TREF, displayed both the HTCP and the VLTCP. This suggests that the polymer chains associated with the HTCP are also related to the VLTCP. D. Wilfong suggested[32] that the HTCP and the VLTCP arise from the crystallization of ethylene rich and hexene/butene rich portions of the macromolecule, respectively. That is, the HTCP can be associated with crystallization of the linear portions of the macromolecule into the chain folded lamellae. Highly branched molecular segments of these lamellae are exiled to the interlamellar or interfacial regions of the crystal and crystallized upon further undercooling.

However, the origin and properties of VLTCP cannot be explained only in terms of the crystallization of ethylene sequences having a relatively short average sequence length. In this case the lamellae population formed at low temperature should be thin[8] and therefore should melt at considerable low temperature. This is not observed for the studied materials. Following the results, presented in Figure 6, the melt topology (in other words, entanglements) also has to be taken into account.

Unfortunately, only DSC experiments without any additional morphological study cannot provide us with full information about structure of crystallites formed at very-low crystallization temperature. It is the body of our upcoming study.

Conclusion

On the basis of the DSC experimental results on low temperature crystallization behavior of SS and ZN based ethylene/α-olefin copolymers the following conclusions can be made:

1) DSC curves uniquely show the presence of an additional crystallization process occurring at very low temperatures around 60–75 °C. This VLTCP 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 VLTCP.
2) The peak crystallization temperature of the VLTCP, T_{VLTCP}, decreases both with increasing comonomer content (if MM is fixed) and with decreasing MM (when comonomer content is approximately constant). At the same time, T_{VLTCP} does not depend on catalyst type used for producing the copolymers.
3) Very slight dependences of the degree of crystallinity calculated from the VLTCP, X_{VLTCP}, on co-monomer content were observed at least within the studied range of magnitude. However, the X_{VLTCP} is independent of the chemical nature of the co-monomers (1-butene or 1-hexene).
4) It was observed that X_{VLTCP} sharply increases with MM in the range of 5–50 kg/mol, and levels off at higher MM. In the same time the crystallinity of HTCP decreases with MM in the range of 5–50 kg/mol. This implies a molecular correlation between the primary and secondary crystallization processes.
5) The X_{VLTCP} is in turn strongly influenced by the type of catalyst. For the SS materials the X_{VLTCP} is higher than for the ZN samples.

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[1] E. T. Hseih, C. C. Tso, J. D. Byers, T. W. Johnson, Q. Fu, S. Z. D. Cheng, *J. Macromol. Sci. - Phys.* **1997**, *36*, 615.
[2] P. J. Flory, *Trans. Faraday Soc.* **1954**, *51*, 848.
[3] I. A. Hussein, *J. Appl. Polym. Sci.* **2008**, *107*, 2802.

[4] V. B. F. Mathot, ''*Calorimetry and Thermal Analysis of Polymers*'', Hanser Publishers, Munich-Germany-Vienna-New York 1994.

[5] V. B. F. Mathot, R. L. Scherrenberg, T. F. J. Pijpers, *Polymer* **1998**, *39*, 4541.

[6] J. Minick, A. Moet, A. Hiltner, E. Baer, S. P. Chum, *J. Appl. Polym. Sci.* **1995**, *58*, 1371.

[7] F. Zhang, J. Liu, F. Xie, Q. Fu, T. He, *J. Appl. Polym. Sci. Polym. Phys.* **2002**, *40*, 822.

[8] F. M. Mirabella, *J. Appl. Polym. Sci.* **2008**, *108*, 987.

[9] A. Alizadeh, L. Richrdson, J. Xu, S. McCartney, H. Marand, *Macromolecules* **1999**, *32*, 622.

[10] H. Teng, Y. Shi, X. Jin, *Polym. J.* **2003**, *35*, 436.

[11] R. G. Alamo, L. Mandelkern, *Thermochim. Acta* **1994**, *238*, 155.

[12] R. G. Alamo, E. K. M. Chan, L. Mandelkern, *Macromolecules* **1992**, *25*, 6381.

[13] E. Ergoz, J. G. Fatou, L. Mandelkern, *Macromolecules* **1972**, *5*, 147.

[14] K. Ziegler, E. Holzkamp, H. Breil, H. Martin, *Angew. Chem.* **1955**, 541 G. Natta, *J. Polym. Sci.* **1955**, *16*, 143.

[15] P. Pino, A. Oschwald, F. Ciardelli, C. Carlini, E. Chiellini, in: ''*Coordination Polymerization of a-Olefins*'', J. C. W. Chien Ed., Elsevier, New York 1975, p. 25.

[16] W. Holtrup, *Makromol. Chem.* **1977**, *178*, 2335.

[17] A. Lehtinen, R. Paukkeri, *Macromol. Chem. Phys.* **1994**, *195*, 1539.

[18] T. Usami, Sh. Takayama, *Polym. J.* **1984**, *10*, 731.

[19] D. Wilfong, G. W. Knight, *J. Polym. Sci., Polym. Phys.* **1990**, *28*, 861.

[20] T. Poltimäe, E. V. Tarasova, A. Krumme, A. Lehtinen, A. Viikna, *Proceedings of the Estonian Academy of Sciences*, *in press*.

[21] M. Kim, P. J. Philips, *J. Appl. Polym. Sci.* **1998**, *70*, 1893.

[22] R. G. Alamo, L. Mandelkern, *Macromolecules* **1989**, *22*, 1273.

[23] L. Mandelkern, *J. Phys. Chem.* **1971**, *75*, 3909.

[24] L. Mandelkern, R. G. Alamo, M. A. Kennedy, *Macromolecules* **1990**, *23*, 4721.

[25] L. Mandelkern, *Acc. Chem. Res.* **1990**, *23*, 380.

[26] U. W. Gedde, J. F. Janson, G. Liljenstrom, S. Eklund, *Polym. Eng. Sci.* **1988**, *28*, 1289.

[27] R. G. Alamo, E. K. M. Chan, L. Mandelkern, I. G. Voigt-Martin, *Macromolecules* **1992**, *25*, 6381.

[28] R. G. Alamo, L. Mandelkern, *Macromolecules* **1991**, *24*, 6480.

[29] L. Mandelkern, *J. Phys. Chem.* **1971**, *75*, 3909.

[30] C. G. Vonk, H. Reynaers, *Polym. Commun.* **1990**, *31*, 190.

[31] M. Peeters, B. Goderis, C. Vonk, H. Reynayers, V. Mathot, *J. Polym. Sci. Polym. Phys.* **1997**, *35*, 2689.

[32] D. L. Wilfong, *Polym. Mater. Sci. Eng.* **1989**, *61*, 743.