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Thermal behaviour and real-time morphology of polyolefin systems

CRYSTALLIZATION AND MELTING BEHAVIOR OF POLYMERIC MATERIALS

1. Introduction

Nowadays, a variety of ethylene based (co)polymers exists which have different molecular architectures [1]. One can distinguish between LPE (linear polyethylene, a strictly linear sequence of methylene groups), HDPE (high-density polyethylene, which is basically linear but with a small degree of short branches), LDPE (low-density polyethylene, which involves both short and long chain branching introduced along a radical route in a high-pressure process), LLDPE (linear low-density polyethylene, involving short chain branching only) and finally a group which can be termed as homogeneous ethylene copolymers. LLDPE and homogeneous ethylene copolymers are produced by the copolymerisation of ethylene with (usually) an α-olefin, which can be either propylene, 1-butene, 1-hexene or 1-octene, giving rise to a short chain branch of 1, 2, 4 or 6 hydrogenated carbon atoms respectively. In the case of LLDPE there are intra- and intermolecular differences with respect to co-monomer amount and distribution along the methylene main chain, whereas this is not the case for homogeneous copolymers. This heterogeneity in the case of LLDPE arises from the use of catalysts with at least two different active sites. Homogeneous copolymers are synthesised nowadays by means of single-site metallocene catalysts.

Thermal behaviour, as revealed by Differential Scanning Calorimetry (DSC), can be used as a product-fingerprint because it strongly depends on molecular parameters such as chain length, chain length distribution and branching. It is day-to-day practice in industry to use DSC for identification, characterisation and product development. DSC, when operated at high scanning rates, is one of the exceptional tools that can be used as a high throughput instrument for the rapid screening and characterisation of extremely low masses of newly developed olefin-based products

Abstract

The thermal behaviour of ethylene based (co)polymers, as revealed by (TM)DSC, can be used as a product-fingerprint because it strongly depends on molecular parameters such as chain length, chain length distribution and branching. To properly understand DSC thermal behaviour, the concomitant changes in phase structure (morphology) and their relationships with the molecular structure and processing history were studied, using independent morphology-sensitive tools under conditions that are DSC-typical. SALLS and the real-time SAXS/WAXD synchrotron allowed for a morphological characterisation from the micrometer to the nanometer scale within time frames of a few seconds. The latter tools were optimised, and new methods for X-ray and light scattering data evaluation were developed. A molecularly well-characterised linear polyethylene, a homogeneous ethylene-1-octene copolymer and a binary blend of these components were investigated. The latter can be considered as a model system for linear low-density polyethylene.

Key words: *crystallisation, polyolefins, synchrotron*

along (for example) combinatorial routes [2]. Besides differences in molecular structure, thermal behaviour is also very dependent on the sample's processing history. Usually a thermal analyst tries to extract such information from a first heating curve in DSC, whereas a second heating curve after a controlled cooling step is used for identification. Finally, since in the processing of such PE products a thermal treatment is involved, one can - at least for that particular, but important part - use DSC to mimic and evaluate processing conditions.

For all these purposes, the time and temperature dependencies of heat capacities and the latent heats associated with phase transitions are evaluated. In the explanation of DSC output, molecular and phase-structural (i.e. morphological) concepts are used which cannot directly be extracted from DSC data. To properly understand DSC thermal behaviour, it is important to study the concomitant changes in phase structure (morphology) and their relationships with the molecular structure and processing history, by using independent, morphology-sensitive techniques under conditions that are DSC-typical.

In this paper, a morphological study is presented involving real-time synchrotron small (SAXS) and wide-angle (WAXD) X-ray and small-angle laser light scattering (SALLS) efforts under conditions typical for DSC and Temperature Modulated DSC (TM-DSC). This combination of experiments allows for

a morphological characterisation from the nanometer to the micrometer scale within time frames of a few seconds. An important part of the work comprises the optimisation and development of new methods for X-ray and light scattering data evaluation. Two molecularly well-characterised samples were used, an LPE and a homogeneous ethylene-1-octene copolymer. A binary blend was investigated as well, and can be considered as a model system for LLDPE. This work considerably sharpened the concepts needed to link thermal behaviour to molecular architecture, sample composition and thermal history. Four characteristic items are discussed below: reversible melting and crystallisation, multiple crystallisation behaviour in the case of a homogeneous copolymer, a copolymer characteristic crystallinity paradox, and the melting behaviour of a 15/85 LPE/Copolymer blend after crystallisation at two different rates.

2. Experimental

2.1. Materials

The LPE and the homogeneous copolymer were prepared at DSM Research using a promoted Vanadium-based catalyst. The LPE (DSM code: JW1114) has a weight average molar mass (Mw) of 52,300 g/mole and a polydispersity (Mw/Mn) of 3. The homogeneous ethylene-1-octene copolymer (JW1120) contains 5.2 mole% 1-octene, has an Mw of 30,800 g/mole and an Mw/Mn of 2.

The blend was prepared by dissolving the two polymers in xylene (15 minutes' reflux at 134.5 °C) at 1% (m/m) followed by co-precipitation into cold acetone at -78 °C. The precipitate was filtered, harvested and dried in a vacuum oven at room temperature for 24 hours. The 15/85 blend discussed below contains 15% LPE and 90% copolymer (mass %).

2.2. Methodology

Time-resolved SAXS and WAXD data were collected using the X33 double focusing camera of the EMBL in HASYLAB at a wavelength of 1.5 Å. This set-up is located at the DORIS storage ring of the Deutsches Elektronen Synchrotron (DESY), Hamburg, Germany [3]. All experimental details have been described earlier together with those for SALLS, WAXD, DSC [4,5] and TM-DSC [6]. Crucial to this study was the development of methods to calculate the overall crystallinity as a function of temperature from synchrotron SAXS patterns. Previously the researcher was limited to the determination of a local crystallinity, which holds for the semi-crystalline regions only. Methods have been developed to cope with samples in which the semi-crystalline regions are surrounded by fully amorphous material (the A-CA model) [4], or in which regions with two different degrees of crystallinity are present (the CA-CA model) [5]. In both models, the semi-crystalline regions consist of isotropically oriented one-dimensional stacks of alternating crystalline and amorphous layers. Both processing procedures can in principle also deal with assemblies of isotropically oriented, isolated crystalline lamellae in an amorphous matrix and with samples that are completely filled with one-dimensional lamellar stacks that have the same crystalline and amorphous layer thickness distributions and stack organisation. Both procedures can thus be used to follow the transformation of an amorphous melt into a homogeneous semi-crystalline morphology. The way in which this is envisaged, however, depends on the model as schematically illustrated in Figure 1. In the A-CA model, isolated lamellae may form first according to (a), leading to (1), and transform according to (b) into an assembly of stacks, i.e. (2). In going from (2) to (3), the crystallinity increases by lamellar insertion (c), stack thickening (d) and the formation of new stacks (e). Finally, space is completely filled with stacks in (4). The crystallinity may further increase by ongoing lamellar insertion leading to (5). The SAXS analysis, according to this model, cannot distinguish between (e) and (d) and the stacks that are formed in (e) are assumed to have the same crystallinity and stack buildup as those that were generated earlier by the sequence (a)-(b)-(c). It is also taken for granted that stacks thicken with a crystallinity equal to the instantaneous crystallinity in the centre of the stack, although this central crystallinity may have been accomplished at earlier times along a more gradual route, i.e. along (a), (b) and (c). In fact, at each time all stacks are assumed to be identical. This differs from the newly proposed CA-CA model in which new stacks are allowed to grow from isolated lamellae, generated between earlier formed stacks as depicted in Figure 1 (2'). Intermediate stages with fractions that have a different crystallinity are possible too, as for example in (3'). At each stage, however, only *two* different fractions are allowed.

SAXS provides structural parameters such as crystalline and amorphous layer thickness in the case of a lamellar morphology. The latter values are related to local crystallinities. For direct comparison with DSC and for consistency, however, a value for the overall crystallinity is needed, since that is the only number provided by DSC. Moreover, a good crystallinity estimate is important in understanding the mechanical properties of these polymeric systems. Methods have been introduced to obtain such values from SAXS data, based on the A-CA as well as on the CA-CA model based on a scaling of the SAXS invariant [4,5]. The overall crystallinity values as obtained are in good agreement with those obtained by DSC and wide-angle X-ray diffraction (WAXD). SALLS experiments are very useful in proving the presence of amorphous areas outside the semi-crystalline regions (A-CA case) or crystallinity heterogeneity (CA-CA case) independently and unambiguously [4,5]. For details on the WAXD and SALLS results, the reader is referred to the literature [4-6].

3. Results

3.1. Reversible melting and crystallisation

An analysis according to the A-CA model seemed appropriate for the LPE sample, cooled and heated at 10 °C/min, which is a standard DSC program [4]. During the first stage of crystallisation, there are amorphous regions outside the semi-crystalline regions because growing spherulites do not fill the space completely. This is apparent from Figure 2 where α, the fraction of semicrystalline regions, is below 1 at the highest temperatures. During melting, a similar picture is obtained since larger amorphous regions develop at high temperatures within the spherulites because of the complete melting of the semi-crystalline stacks.
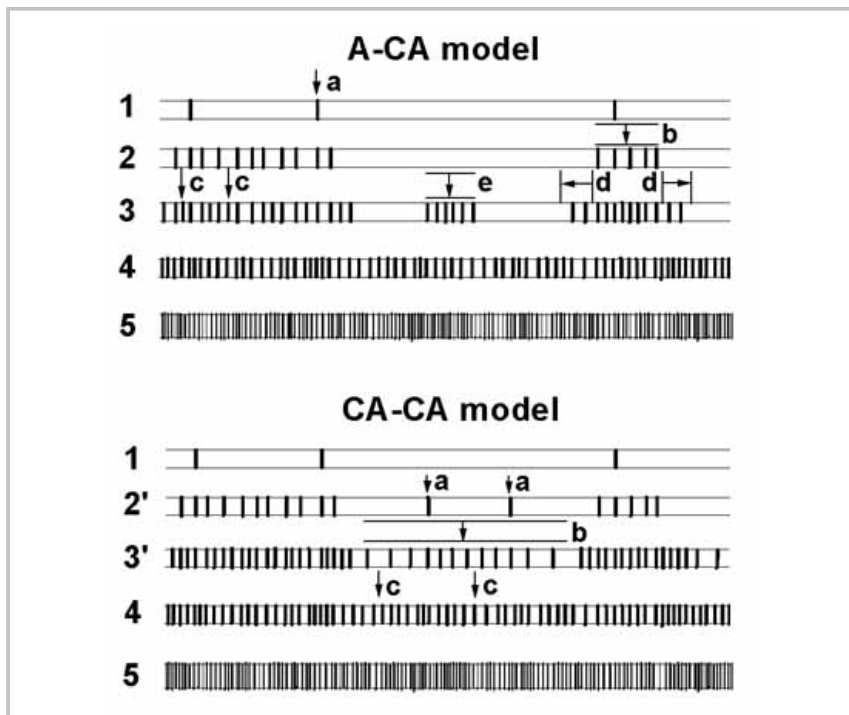
Figure 1. Comparison of the structural evolution assumed in the A-CA and CA-CA models. Steps in the morphology development are numbered, whereas the processes involved are labelled with letters. The thin vertical black lines represent edge-on lamellar crystals that are generated in a horizontal one-dimensional stack.

From Figure 2 it is clear that the SAXS crystallinity evolution very closely follows that based on DSC. The slow crystallinity increase after the spherulites have become space-filling is entirely due to an increase of ϕ. The long period (*LP*) in that temperature range does not change, and hence indicates at crystallite thickening during crystallisation as illustrated in Figure 3 . The latter data are based on an analysis of correlation functions according to the A-CA model [4]. The process is reversed upon heating (Figure 3). Surface melting occurs between room temperature and the end melting temperature, giving rise to endothermic heat change without the complete melting of lamellae. Complete melting, revealed by an increase of the long period (*LP*), only occurs at the highest temperatures. There is recrystallisation followed by isothermal lamellar thickening if annealing steps are inserted [7,8].

In the case of LPE, surface melting and crystallisation is the key mechanism behind reversible melting and crystal-lisation, as proved by TM-DSC [6]. In contrast to classical DSC, TM-DSC allows the determination of the heat capacity as a function of time during a (quasi)-isothermal run. Quasi-isothermal differs from 'isothermal' because of a small temperature modulation that is superimposed. The quasi-isothermal melt crystallisation of an LPE sample at 126°C was monitored by TM-DSC and the associated structural changes by the synchrotron WAXD and SAXS [6]. The results of this experiment are summarised next [6]. Crystallisation is mainly irreversible, i.e. the crystallinity progressively increases with time. The instantaneous crystallisation rate, however, depends on the actual temperature: a decrease is observed with increase in temperature within a cycle. The lamellar crystals irreversibly thicken with time. Superimposed upon this overall thickening process, a small reversible change is observed out of phase with the temperature excursions; in other words, the crystal thickness (T_c) slightly decreases with increasing temperature, and vice versa.

A similar observation can be reported for a TM-DSC like melting experiment. Figure 4 displays the evolution of T_c, and also illustrates the used temperature program. The LPE sample was cooled at 10°C/min prior to this modulated heating experiment.

Up to 35 min (about 115°C), T_c decreases with a small superimposed oscillation out of phase with that of temperature. This once more illustrates the reversible character of fold surface melting and crystallisation. Over longer times (higher temperatures), the crystals start to thicken. This irreversible thickening is an annealing effect associated with the relatively long residence time at each temperature. After all, the underlying heating rate is only 1°C/min. This thickening can be avoided by increasing the heating rate. Figure 5 shows the evolution of T_c as a function of temperature, together with the evolution of T_c when heated at 10°C/min without the application of a temperature modulation. In the latter case, surface melting continues even beyond 115°C, and
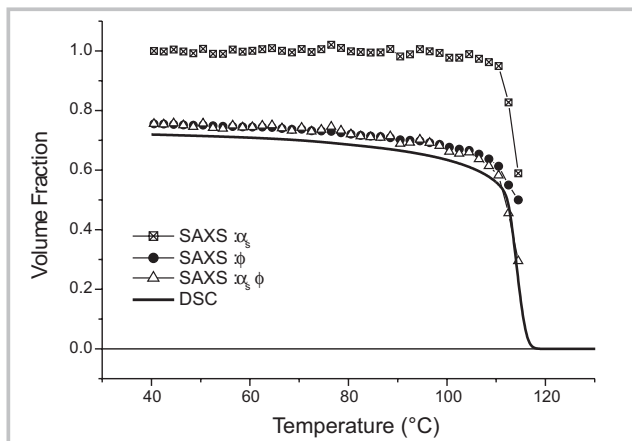

Figure 2. *Comparison of the SAXS crystallinity estimates (ϕ, local stack crystallinity; α fraction of stacks, $\alpha\phi$ total crystallinity) compared to the crystallinity obtained by DSC (mass fraction is converted into volume fraction [3]).*

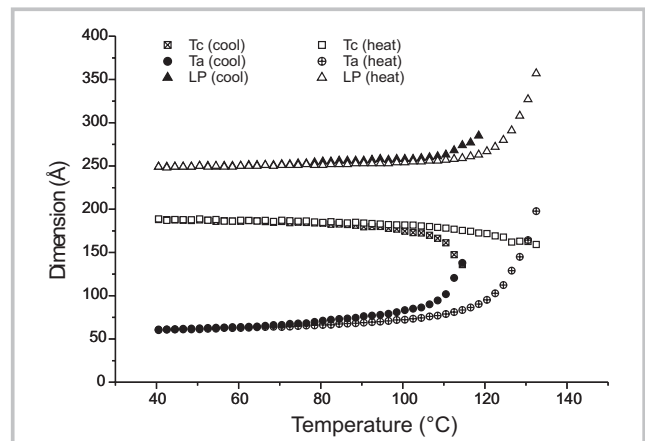**Figure 3.** *The evolution of the lamellar thickness (Tc), the amorphous layer thickness (Ta) and the long period (LP) during cooling and heating at 10°C/min. [3].*
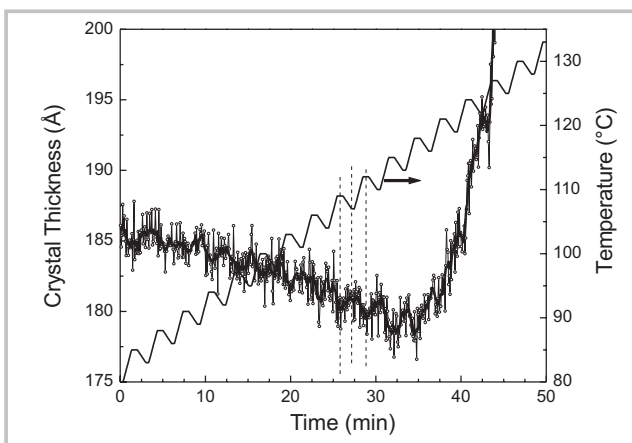

Figure 4. *Evolution of Tc during the melting of a linear polyethylene heated according to the temperature program illustrated by the oscillating full line. The thick full line represents a smoothing of Tc by a seven-point averaging. The dashed lines are guides to the eye.*
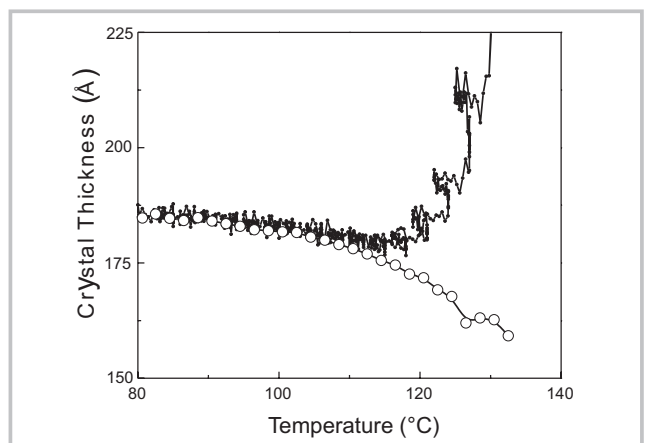

Figure 5. *T_c data of Fig. 1 but plotted as a function of temperature (small connected closed circles). The large open circles represent the evolution of T_c when heated at a rate of 10°C/min. Both samples where cooled at 10°C prior to heating.*

crystal thickening is not observed. Note that the irreversible thickening essentially occurs during the heating step of a temperature cycle. During subsequent cooling, T_c slightly decreases for reversible fold surface activity, as expected.

An analysis of the total scattering power reveals that, when crystals start to thicken, there is some concomitant irreversible melting involved, which gains importance with increasing temperature.

3.2. Multiple crystallisation behaviour in the case of a homogeneous copolymer

The CA-CA model approach was applied to the homogeneous ethylene-1-octene copolymer in a cooling and heating cycle at 10°C/min [5]. DSC and SALLS point to 94°C as the onset temperature for crystallisation as illustrated in Figure 6 for DSC. The initial sharp DSC exothermic peak is associated with the process of primary crystallisation. The crystallinity distribution inside the spherulites at impingement is asymmetric, with a most probable local crystallinity of 18% and with about 10% of the spherulite internal volume remaining amorphous. Upon further cooling, crystallinity develops more rapidly in the least crystalline regions compared to areas where crystals are more closely packed. As a result the crystallinity distribution becomes progressively symmetric. The crystallinity is homogeneously distributed over the sample volume at and below 70°C, and further increases slowly by insertion of new crystals. At 50°C this process accelerates, probably due to the onset of homogeneous nucleation. The crystals involved are either small or very imperfect because they do not contribute to the WAXD crystalline reflections. The average thickness of the crystals remains constant during cooling and heating, with, however, a slight increase at the end of the heating run, which is taken as evidence for melting and recrystallisation into thicker crystals. The crystals that were formed during previous cooling melt in the reverse sequence of their formation, since the evolution of *LP* as a function of temperature during heating is comparable to that of the cooling experiment, taking hysteresis into account. This hysteresis can also be observed in the evolution of most volume fraction estimates. The only difference between heating and cooling occurs at the highest temperatures, where the process of primary crystallisation is not reversed since spherulites, obviously, do not melt back towards their primary nucleus. Spherulite melting is, however, a very heterogeneous process, during which regions with different degrees of crystallinity develop.

3.3. The crystallinity paradox

The melting behaviour of the copolymer during heating at 10°C/min, either after cooling at 0.1°C per minute (slow cooling) or quenching into liquid nitrogen, is rather exceptional [7]. The DSC crystallinity evolution of these samples is illustrated in Figure 7. Clearly, there is a temperature window (1) in which the crystallinity of the quenched sample exceeds that of the slowly cooled sample.

Here the A-CA approach was used again to analyse the SAXS linear correlation functions. At first ϕ decreases during heating but at high temperature ϕ increases, whereas the DSC crystallinity data does not. In these high temperature regions, the semi-crystalline regions no longer fill up space completely, and fully amorphous zones are present outside the lamellar stacks, i.e. $\alpha < 1$ as illustrated in Figure 8.

Apparently this homogeneous copolymer does not melt entirely homogeneously over the volume. The overall SAXS crystallinity (Figure 8), $\alpha\phi$, of the quenched sample exceeds that of the slowly cooled sample during heating, similar to the DSC crystallinity values in Figure 7. This is in part due to the earlier decrease of α, but for the most important part is due to the faster decrease of ϕ, caused by the faster increase of T_a, for the slowly cooled (compared to the quenched) sample as illustrated in Figure 9.

The Tc values increase with temperature, as illustrated more clearly in figure 10. Over the entire melting range, T_c of the quenched sample is lower than that of the slowly cooled counterpart even at and beyond the melting peak temperatures, which -(very surprisingly) for the quenched sample equals 101°C, and 98.8°C for the slowly cooled sample.

The following line of thought allows us to account for the higher melting peak temperature after quenching. During *slow cooling*, separate crystals are formed according to ethylene sequence length by a process of fractionation. Hexyl branches, originating from the incorporation of 1-octene in the PE chain, cannot be incorporated into the crystal lattice. According to *nucleation theory*, at the highest temperatures only relatively thick lamellar crystals can be formed involving only relatively long ethylene sequences. Shorter ethylene sequences are segregated from the crystallisation front, but are able at lower temperatures to crystallise into thinner crystals. During subsequent heating all crystals melt in the reversed sequence of their formation. DSC shows a broad endothermic signal, and T_c increases because of the selective melting of thinner crystals. T_a and *LP* increase more rapidly. During *quenching*, crystallisation occurs at a much larger supercooling. Sequences of
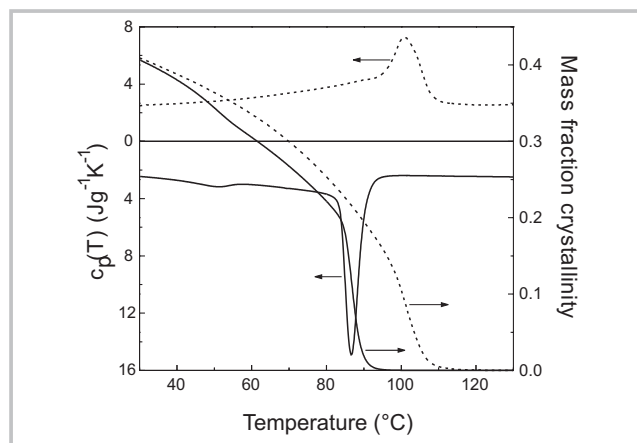

Figure 6. DSC cooling (full line) and heating (dashed line) $c_p(T)$ curves recorded at 10°C/min for the homogeneous copolymer, together with the DSC-based crystallinity values represented with corresponding line types.
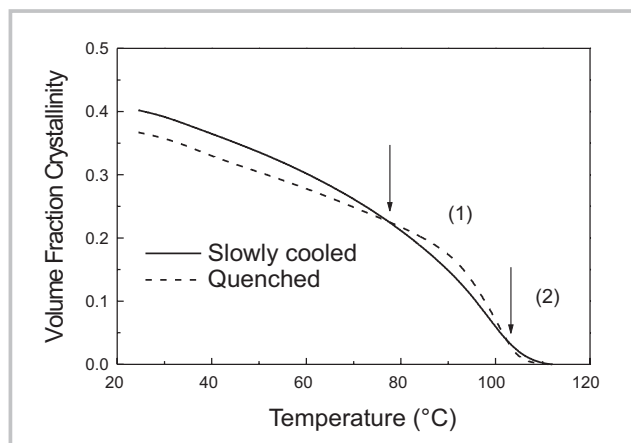

Figure 7. DSC-based crystallinity evolution of the copolymer after cooling at two different rates (heating rate is 10°C/min).

different length *co-crystallise* as relatively thin, imperfect and unstable but uniform crystals. If the quenched samples are heated, the unstable (co)crystals melt after the slightest increase of temperature. Nearly all ethylene sequences are released at the same time, and recrystallisation follows instantaneously since the temperature is relatively low, and the supercooling is consequently large. These new crystals are still rather imperfect and there is considerable *co-crystallisation*. The shortest sequences, released from the original crystals, no longer participate in this crystallisation because of the higher temperature. Melting of these new crystals occurs again at slightly higher temperatures, and again most of the sequences are released. Recrystallisation follows, where slightly longer sequences are excluded as well. This process of melting and recrystallisation repeats until crystals are formed that melt at such a high temperature that recrystallisation is no longer possible during the time allowed in the heating process. Crystallisation at high temperatures is slowed down because of decreased supercooling, and secondly because sufficiently long ethylene sequences become rare. The endothermic DSC signal partially overlaps with the exothermic signal of recrystallising material, resulting in a narrow melting region and a peak at a relatively high temperature, i.e. higher than in the case of a slow cooling process. Clearly, the melting peak temperature of copolymers cannot be used to estimate the perfection or thickness of the crystals formed during cooling.

Besides a minimum ethylene sequence length for crystallisation at a given temperature, a minimum amount of refolding chains is also needed in order to avoid a density conflict. In the case of copolymers there is a potential *overcrowding* [9-11] of leaving chains, since hexyl branches are expelled from the crystal [12]. According to Vonk [10], at least 60% of the stems reaching the surface of a PE crystal have to bend back into the crystal of origin. For this reason, an amount of the ethylene sequences which have the critical length for nucleation at a given temperature (but which are only a few times this length) are nevertheless expelled and do not participate in the crystallisation. Such sequences can, however, crystallise at that specific temperature provided they *co-crystallise* with longer sequences. The latter are able to crystallise with a re-entry loop, giving rise to a lower number of leaving chains at the crystal surface (i.e. overcrowding is avoided). During *slow cooling*, an amount of (shorter) ethylene sequences with potential for crystallisation at a given temperature remain amorphous, because longer sequences are consumed in the crystallisation at higher temperatures, and co-crystallisation is impossible. These sequences crystal-lise at lower temperatures, where thinner crystals can be formed and slightly shorter ethylene sequences can crystallise with a re-entry loop (without overcrowding problems). During subsequent heating, overcrowding also prevents recrystallisation of slowly cooled samples. At each temperature, an amorphous fraction is generated in which no long sequences are available for co-crystallisation since they are still built into crystals that melt at higher temperatures. T_c of the slowly cooled copolymer is always larger than that of the quenched sample, as illustrated in Figure 10. In contrast, during heating after *quenching*, extensive co-crystallisation is involved as sketched above. These crystals contain a high fraction of relatively short ethylene sequences because the longer sequences are present in the same crystal and overcrowding does not occur. The relatively higher mass fraction of crystallised ethylene sequences causes
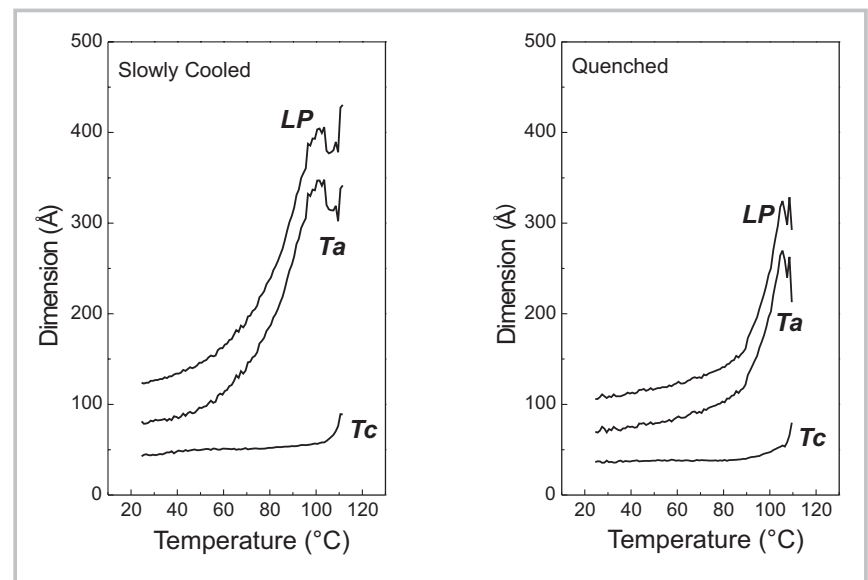

Figure 9. Evolution of LP, T_c and T_a during heating at 10°C/min after slow cooling (left) and quenching (right).
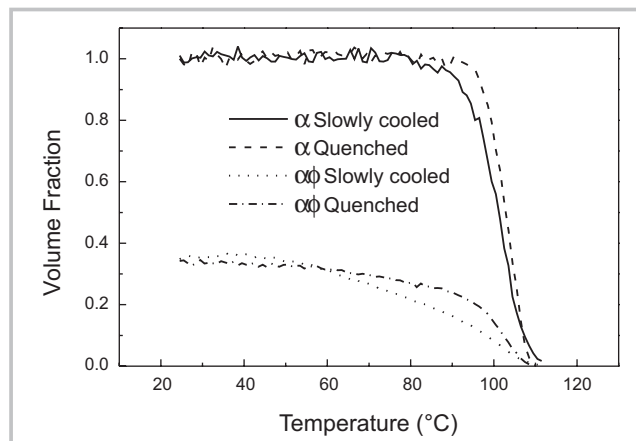

Figure 8. SAXS-based overall crystallinity, $\alpha\phi$, and fraction of semi-crystalline regions, α, after cooling the copolymer at different rates.
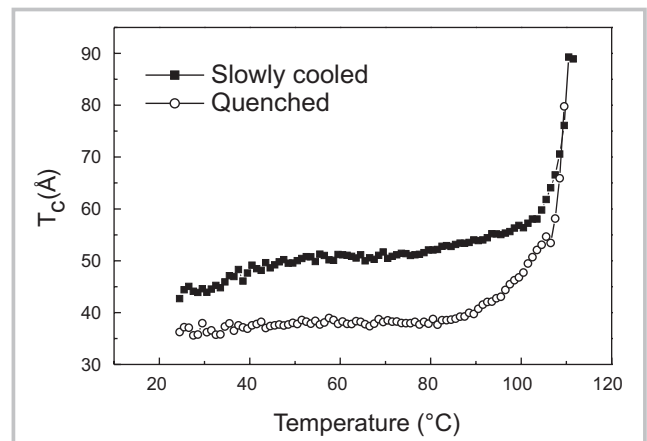

Figure 10. Evolution of T_c during heating the copolymer at 10°C/min.

higher crystallinity in the temperature window labelled (1) in Figure 7. In the temperature region below (1), all sequences with a potential for crystallisation are (to some extent) in the crystalline state because of the low temperatures. The amount of ethylene sequences in (co)crystals is below the amount incorporated by slow cooling. In the temperature region labelled (2) in Figure 7, the crystallinity of the S-samples is also above that of the Q-copolymers. At these high temperatures only relatively thick crystals are stable, which can be formed after sufficient time at high temperatures, i.e. in a slow cooling process, and apparently not by recrystallisation during heating. As mentioned above, (re)crystallisation at high temperatures is slow, because of small supercooling and because sufficiently long ethylene sequences for nucleation are rare.

The selection process of ethylene sequences and the concomitant spatial segregation of material during slow cooling is reflected in the earlier decrease of α during melting compared to the quenched sample (Figure 2).

The lamellar crystals of the slowly cooled sample melt in the reverse order of their formation, i.e. the crystals melt according to their thickness. Quenching creates unstable crystals through co-crystallisation of ethylene sequences with different lengths. These crystals repeatedly melt and (co-)recrystallise during heating. The exothermic heat change due to recrystallisation partially compensates the endothermic heat change associated with melting, resulting in a narrow overall DSC melting peak with its maximum at a higher temperature than the melting peak of slowly cooled copolymers. With increasing temperature, the crystallinity of quenched copolymers overtakes that of the slowly cooled samples due to co-recrystallisation. Within a given temperature window during heating, a higher crystallinity can be obtained by cooling a copolymer more rapidly prior to heating.

3.4. The melting behaviour of an LLDPE-like blend

A 15% LPE and 85% copolymer blend was studied during heating at 10°C/min. The melting after cooling at 10°C/min was compared to that after quenching into acetone at freezing point. Cooling at 10°C/min was also considered. During cooling, the LPE fraction crystallises first to form space-filling spherulites of low crystallinity with the amorphous copolymer segregated into small separate regions. This copolymer fraction

crystallises later upon further cooling. During heating the sequence of events is reversed, but part of the LPE fraction recrystallises at high temperatures. Quenching results in co-crystallisation without pronounced component segregation. Segregation, however, occurs during heating as these (co)crystals melt and recrystallise. Increasingly longer copolymer ethylene sequences are progressively excluded from the recrystallisation process while temperature is increased. This recrystallisation is very fast and cannot be avoided fully by increasing the DSC heating rate. The same reasoning as given above for the pure copolymer sample accounts for the higher crystallinity of this blend sample after quenching compared to after cooling at 10°C/min.

4. Conclusions

The aim of this work was to gain a better understanding of the relationships between polyethylene chain microstructure, thermal history, thermal behaviour and morphology. Emphasis was placed on the morphological changes during the thermal treatments that are frequently met in (TM) DSC measurements. A combination of synchrotron X-ray and laser light scattering methods was used to follow the structural changes from the nanometer to the micrometer scale within time frames of a few seconds. The use of linear correlation functions to analyse small-angle scattering curves of two phase crystalline-amorphous lamellar systems was extended to account for morphological effects that typically show up at high temperatures during either cooling or heating. Methodologies were developed based on two different models: the A-CA and CA-CA models.

Crystals thickening during cooling at 10°C/min. and surface melting upon heating are observed for LPE, which accounts for the broad exothermic or endothermic low temperature shoulders of the DSC crystallisation and melting peaks and for the reversible melting and crystallisation phenomena observed by (TM)DSC. The initial sharp exothermic DSC peak observed when a copolymer is cooled at 10°C/min. is related to the process of primary crystallisation: the growth of spherulites until impingement. The crystallinity in these spherulites is initially very low, but increases when new crystals are formed in the spherulites upon further cooling. When a copolymer is cooled slowly, crystals of decreasing thickness are formed with decreasing temperature. The thickest crystals consist of the longest ethylene sequences. Crystals melt according to

their thickness upon heating, and a broad endothermic DSC peak is observed. By quenching, ethylene sequences of different length co-crystallise into relatively thin crystals, which upon heating repeatedly melt and recrystallise. The crystallinity of quenched samples overtakes that of slowly cooled copolymers, since there is also co-crystallisation of ethylene sequences with different lengths during recrystallisation. The result for DSC is a fairly narrow melting peak, because the exothermic heat change associated with recrystallisation partially overlaps the endothermic melting signal. Similar effects are observed for an LPE/copolymer blend. By quenching, the blend components co-crystallise, but segregation occurs upon heating by melting and selective recrystallisation. The components crystallise separately if cooled more slowly, and the crystals melt in the reversed order of their formation upon heating. The presented experimental results and their interpretation enable a more adequate interpretation of the DSC output.

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