

S. Rabiej,<sup>1</sup> B. Goderis,<sup>2</sup>  
J. Janicki,<sup>1</sup> V. B. F. Mathot,<sup>2</sup>  
M. Koch,<sup>3</sup> H. Reynaers,<sup>2</sup>  
A. Wlochowicz<sup>1</sup>

<sup>1</sup>University of Bielsko-Biala,  
43-309, ul. Willowa2, Bielsko-Biala, Poland,  
srabiej@ath.bielsko.pl,  
jjanicki@ath.bielsko.pl,  
awlochowicz@ath.bielsko.pl

<sup>2</sup>Catholic University of Leuven, Laboratory of  
Macromolecular and Structural Chemistry,  
Celestijnenlaan 200F,  
B-3001, Heverlee-Leuven, Belgium,  
bart.goderis@chem.kuleuven.ac.be,  
vincent.mathot@chem.kuleuven.ac.be,  
harry.reynaers@chem.kuleuven.ac.be

<sup>3</sup>European Molecular Biology Laboratory  
EMBL c/o DESY,  
Notkestrasse 85, D-22603 Hamburg, Germany  
Michel.Koch@embl-hamburg.de

# Influence of thermal treatment on the supermolecular structure of homogeneous polyethylene-1-octene copolymers

## Abstract

DSC & simultaneous real-time SAXS and WAXS studies of the isothermal crystallisation, melting and morphology of homogeneous polyethylene-1-octene copolymers are presented. The multiple melting behaviour of the copolymers observed after isothermal crystallisation indicates that two kinds of crystals of different stability are formed. Two melting endotherms appear after different periods of isothermal crystallisation, testifying that the melting-recrystallisation-remelting process is not responsible for the effects observed. The crystals which melt at higher temperatures are probably formed from the longest ethylene sequences and are of the lamellar type, while the crystals which melt at lower temperatures are formed from the shorter extended sequences and are of a fringed micelle type.

**Key words:** homogeneous copolymers, isothermal crystallisation, multiple melting, SAXS, WAXS,

## 1. Introduction

The presence of local structural constraints in the molecular chains of polymer during its solidification considerably affects the process of its primary crystallisation, controls its extent and influences the crystallisability of the amorphous phase remaining after the first stages of crystallisation. Such specific constraints exist in copolymers composed of crystallisable and noncrystallisable comonomers, of which homogeneous polyethylene-1-octene copolymers may serve as an example. In these copolymers, short hexyl branches randomly distributed along the polyethylene chain generate a distribution of ethylene sequences of different lengths which are able to crystallise. Obviously, the kinetics of crystallisation and the morphology of crystals originating during solidification are dependent on the sequence length distribution. This dependency is also reflected in the thermal behaviour of copolymers. This work presents the results of studies on the morphology changes and the behaviour of homogeneous polyethylene-1-octene copolymers during thermal treatment. In our studies we made DSC and simultaneous real-time SAXS and WAXS investigations of their isothermal crystallisation and melting after crystallisation at different temperatures and for different times.

## 2. Experimental

The copolymers were synthesised at DSM Research (the Netherlands) using

a vanadium-based catalyst. Their molecular characterisation as provided by the producer is shown in Table 1.

Investigations were carried out using DSC and time-resolved, simultaneous SAXS and WAXS techniques. Synchrotron X-ray measurements took place in DESY in Hamburg (Germany). The X33 double focusing camera working at the wavelength of 1.5 Å of the EMBL in HASYLAB on the DORIS storage ring was used. The samples with the thickness of 1mm were sealed between thin aluminium foils. The main temperature program to which the samples were subjected consisted in isothermal crystallisation at a fixed temperature after cooling from the melt, followed by cooling to room temperature and subsequent remelting. Crystallisation was performed at two different temperatures, 95°C and 102°C, over different times from 2 min to 90 min. In a reference program, the sample was cooled from the melt directly to the temperature at 10°C/min, and next after about 5 min. it was reheated at the same rate to 150°C. The temperature of the samples during X-ray investigations was controlled by a Mettler FP-82MT hot stage. The SAXS and WAXS data processing was preceded by introductory calculations, i.e. correction, normalisation, and calibration. All of

these, as well as most of the later calculations based on SAXS and WAXS data, were performed using an Otoko computer program [1].

The DSC measurements were performed using Pyris 1 from Perkin-Elmer. The masses of samples varied from 7 to 12mg, and were placed into standard aluminium pans. All measurements were corrected for the instrumental effects by subtracting an empty pan measurement in the same temperature range. DSC thermograms normalised with sample mass and heating rate were used in the calculations of the mass fraction crystallinity  $x_M(T)$  as a function of temperature by employing the Mathot method [2].

## 3. Results

The SAXS data were interpreted assuming a lamellar stacks model. Using the correlation function [3], the thicknesses of crystalline and amorphous regions were determined as well as the long period. Moreover, the fraction of copolymer volume occupied by lamellar stacks [4] and the mass fraction crystallinity were calculated. Based on the WAXS reflections [110] and [200], the dimensions of the unit cell of the copolymer and its volume were calcu-

Table 1. Characteristic of the sample.

Sample	mol % octene	CH <sub>3</sub> / 1000C	M <sub>w</sub> (weight average molar mass)	M <sub>w</sub> /M <sub>n</sub> (polydispersity)
JW1120	5.2	22.5	30 800 [g/mol]	2

lated. In addition, the sum of integral intensities of these reflections was used as an index of crystallinity. During crystallisation at 95°C, the parameters of lamellar stacks change mostly in the first 5-7 minutes, as seen in Fig. 1. The long period decreases from about 310 Å to 270 Å, and the amorphous layer from 260 Å to 220 Å. This decrease in the long period and amorphous layer thickness is caused by the appearance of new crystalline lamellae between the older ones, separated by the amorphous phase. The changes in the thickness of crystalline lamellae are rather random, and remain within the limits of experimental error. Their average value is equal to 48 Å. At the same time, the mass fraction crystallinity increases. During the first 5-7 min. we observe the fastest increase of this parameter. Next, it continues to increase but much more slowly, reach-

ing a nearly constant level after about 20-30 minutes. Such a behaviour can be seen in Fig. 2, which shows the mass fraction crystallinity calculated from DSC and WAXS data. In this figure, the WAXS crystallinity index was scaled to the level of the DSC data in the range of 40-70°C.

The DSC melting curves registered after the isothermal crystallisation change considerably, depending on the time of crystallisation as seen in Fig. 3. The scan for the sample of zero crystallisation time is given here for comparison. This thermogram shows a broad melting peak with a maximum at about 101°C. In the remaining curves we observe two melting peaks. After only 2 min. of crystallisation, the melting peak is shifted to higher temperatures and it is clearly broader. At the same time, a low temperature peak

appears as a small shoulder on its left side. For longer times, the high-temperature peak stabilises at 104°C, increasing only very slightly with time. On the other hand, a low temperature peak localised at 97-99°C grows considerably following a deep minimum in the heat flow rate which lies close to the crystallisation temperature of 95°C. This minimum indicates that melting rate of copolymer decreases considerably at this temperature. Apparently the crystallites which were formed at 95°C must be more perfect or larger, so they melt at higher temperatures. The decrease in the melting rate is also visible in the plot of DSC crystallinity versus temperature during heating. One can see a hump on the curve appearing at 95°C which grows with the time of crystallisation. The crystallinity level at which the hump appears, for the longest crystallisation time (60 min) amounts to 16% (Fig. 5). This value is in very good agreement with the upper level of DSC crystallinity as calculated in the isothermal step (see Fig. 3.).

The hump at 95°C is also visible in the SAXS and WAXS data. Fig. 5 shows the volume fraction of copolymer occupied by lamellar stacks ( $\alpha_s$ ) as well as the SAXS and DSC crystallinities ( $x_M$ ) related to the heating run after 60 min. of isothermal crystallisation. Similar effects during melting can also be observed for the sample crystallised at 102°C (Fig. 4). In this case, the crystallisation time must be longer in order to give noticeable effects. After about 15 min. a small peak appears at 111°C, which increases a little with crystallisation time. After 30 min. a minimum appears, followed by the next peak which increases considerably with time. As before, the minimum is in the vicinity of the crystallisation temperature of

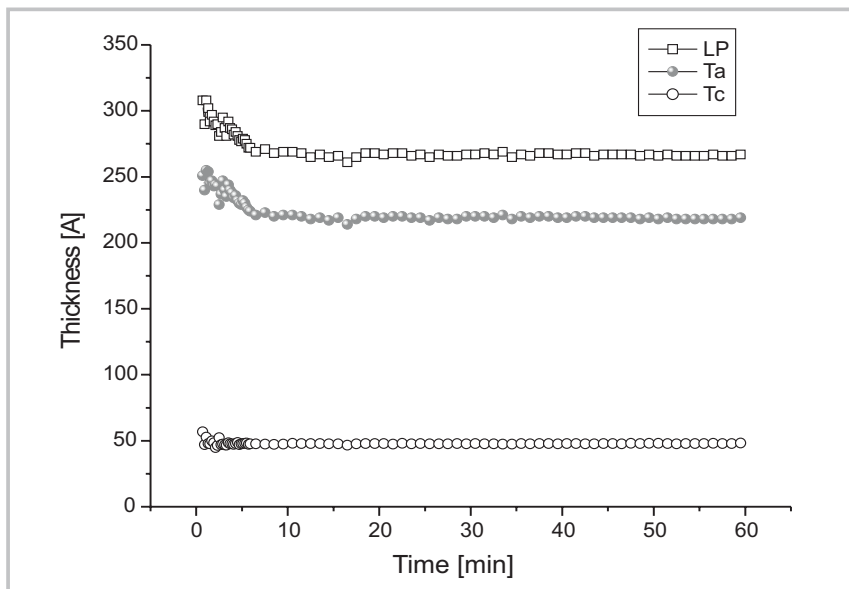


Figure 1. Long period (LP), amorphous (Ta) and crystalline (Tc) layer thicknesses during isothermal crystallization at 95°C.

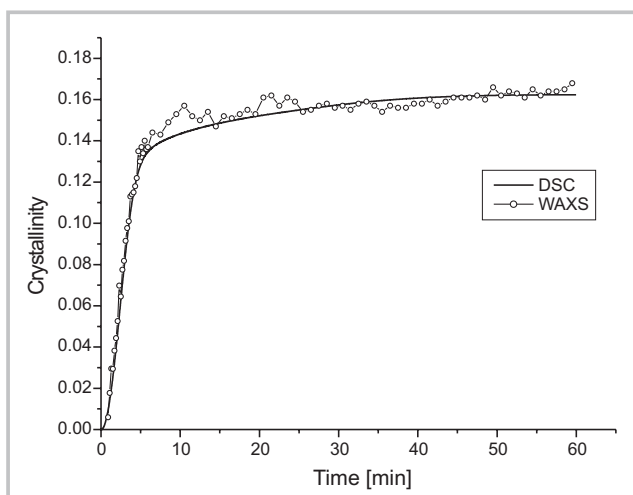


Figure 2. DSC mass fraction crystallinity and WAXS crystallinity index during isothermal crystallization at 95°C

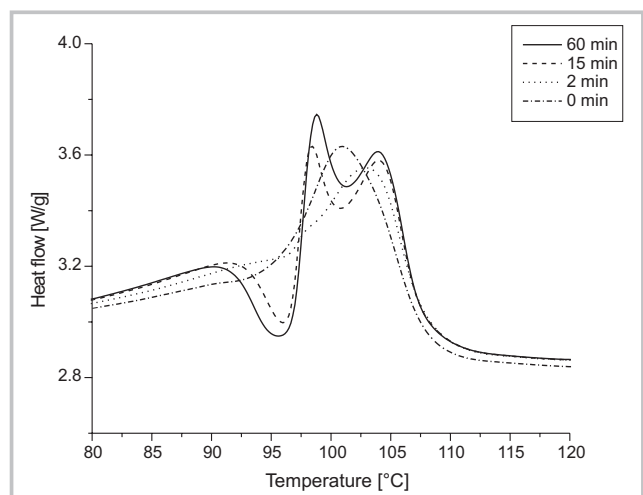


Figure 3. DSC scans for heating from 25°C to 150°C after isothermal crystallization at 95°C for different periods of time (given in the Figure).

102°C, so it must be related to the higher perfection of the crystals formed during crystallisation. The decrease in melting rate is also reflected in DSC, SAXS and WAXS crystallinity plots resulting in a hump localised close to the crystallisation temperature. The multiple melting behaviour, after both the 95°C and 102°C isotherms, is clearly dependent on the heating rate used in DSC scans.

This effect is shown in Fig. 6. The heating rate dependency would suggest melting–recrystallisation–remelting as the source of two peaks observed during heating of the copolymers. However, a careful analysis of the DSC curves, as well as some SAXS and WAXS results, leads to another interpretation.

#### 4. Discussion

Analysing the DSC scans for heating after isothermal crystallisation (Fig. 3), we have to emphasise first of all that the peaks observed during heating do not appear at the same time. The high temperature peak develops sooner than the low temperature one. It means that crystals melting at higher temperatures are generated first, at the beginning of crystallisation. The crystals related to the low temperature peak develop more slowly. However, these predominate later. The difference in melting temperatures indicates the difference in the perfection or size of the crystals. The high temperature peak must come from the more stable crystals that are formed from the longest ethylene sequences.

From the plot of the DSC crystallinity versus time during the isothermal crystallisation at 95°C (Fig. 2), we can esti-

mate that after 2 min. of crystallisation, the crystallinity equals 4.3%. Now, using the plot of the crystallinity versus temperature during heating after 2 min. of isothermal crystallisation, one can read out the temperature to which the copolymer had to be heated in order to reduce its crystallinity to the level of 4.3%. This temperature equals 104.4°C, i.e. it is almost 10°C higher than the temperature of crystallisation. This means that the crystals formed during these 2 min. must be much more stable than those related to the low temperature peak.

The low temperature peak comes from less stable crystals. They are not only smaller but more defective probably because their melting temperature is only about 3°C higher than the crystallisation temperature. As we can see, the population of these crystals increases considerably with crystallisation time at both temperatures.

During the heating run, after the isotherm at 95°C, part of the less stable crystals which melt closest to the crystallisation temperature recrystallise, due to which an exothermic minimum appears in the DSC curve and distorts its shape. New crystals melt once again at about 104°C. The height and shape of the melting peaks is now changed by the effects of recrystallisation and remelting. One may assume that the small increase of the high-temperature melting peak which takes place for longer crystallisation times is only due to the remelting of recrystallised crystals.

Thus, the increase in total crystallinity which takes place after the second minute is only due to the appearance of these less stable crystals. The

number of larger crystals is established at the very beginning of crystallisation. It is easy to notice that the low temperature peak not only grows with time, but also moves very slightly to higher temperatures. This is a typical sign of the reorganisation occurring in the thin crystallites while annealed at high temperature.

Similar conclusions can be derived from the analysis of the DSC melting curves registered after the isothermal crystallisation at 102°C. More stable crystals originate only during the first minutes of the isothermal crystallisation. The increase in the amplitude of the high temperature peak observed in the melting curves between 15 and 90 min. is due only to remelting of the smaller crystallites which had formerly recrystallised during heating. All the time during crystallisation, the low temperature endotherm moves to higher temperatures, indicating the reorganisation of the less stable crystallites.

So to summarise, we can state that the information on the bimodal distribution of the crystallites that we obtain from DSC melting curves is to some degree covered by the thermal effects of recrystallisation and remelting. Due to the presence of these effects, DSC heating curves are influenced by the heating rate. Nevertheless, thanks to the delay in the appearance of the two population of crystallites, they can be recognised using the DSC method.

The SAXS data shows no changes in the thickness of crystalline lamellae during the isothermal crystallisation. (Fig. 1). Based on this fact, we may conclude that the two populations of crystals revealed by the DSC data must dif-

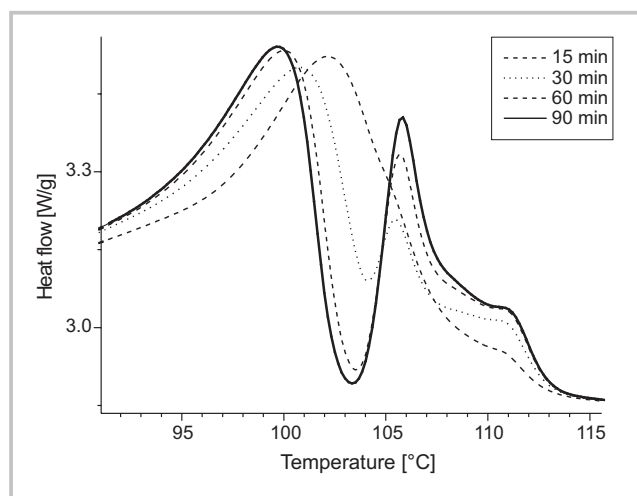


Figure 4. DSC scans for heating from 25°C to 150°C after isothermal crystallisation at 102°C for different periods of time (given in the Figure).

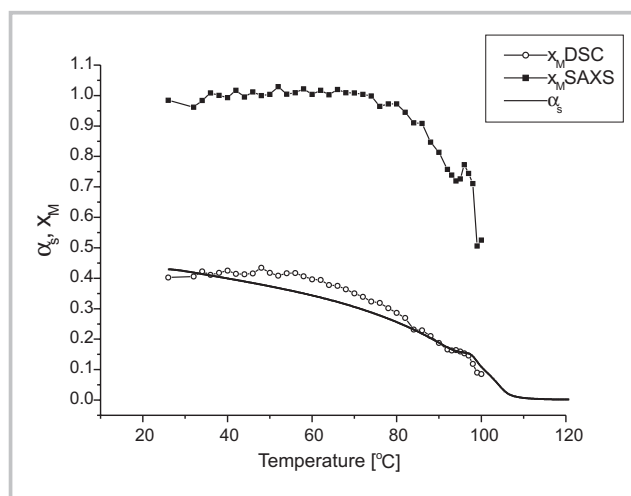


Figure 5. Volume fraction of lamellar stacks  $\alpha_s$  in the copolymer and mass fraction crystallinity ( $x_M$ ) calculated from DSC and SAXS data during heating from 25°C to 150°C after isothermal crystallisation at 95°C for 60 min.

fer in their internal perfection and lateral dimensions, but the thickness of all crystals generated at a given temperature is the same. The more stable crystals are formed from the longest ethylene sequences, which due to larger undercooling crystallise first. These sequences are long enough to form chain-folded, lamellar crystals. At the next stage, when most of the long sequences are incorporated in lamellar crystals, the more branched ethylene sequences crystallise, forming crystals composed of short, extended ethylene sequences with very rare chain folding. The lateral size of these crystals is very limited due to the overcrowding effect. They are of a fringed micelle type.

The phenomenon of multiple melting during the isothermal crystallisation described in this paper has already been reported by other authors [5-9]. The interpretation of the effects observed has been presented by Alizadeh et al. [5] and Crist & Claudio [6] as testifying to the appearance of two different populations of crystallites. Based on DSC data only, Crist & Claudio suggested that the crystals melting at higher temperature are thicker than the fringed micelles. During heating the lamellar crystal thicken, thus increasing their stability and perfection. On the other hand, the thickening of the thinner crystallites is considerably limited by large concentration of branches. However, our SAXS data shows that all crystals have the same thickness, and that no thickening takes place during crystallisation. According to our data, the differences in melting temperatures are related to the internal structure and lateral sizes of the lamellar crystals and fringed micelles. When proposing such an explanation, one may expect these two different

types of crystals to differ in their crystalline structure, i.e. in the lattice constants and unit cell volume. These expectations have good confirmation in the results of our WAXS measurements. It was found that the volume of polyethylene unit cell clearly changes with time during isothermal crystallisation at 95°C. At the first stage it increases, reaching a maximum at about 30-40 min., and then it starts slowly to decrease. This behaviour can be interpreted in the following way. During the first stage, the generation and perfection of the lamellar crystals that appeared at the beginning of crystallisation take place. Due to this, the unit cell volume is relatively small and density high. The fringed micelles that appear later are certainly less perfect and less dense than the reorganised lamellae. Thus, the average unit cell volume starts to increase with time as the number of micelles increases. However, after about 30-40 min. the crystallinity approaches its upper level and grows very slowly, as seen in Fig. 2. From this time, only very few new crystals appear. Due to the reorganisation which occurs in the crystals annealed for a long time at high temperature, their perfection increases and the average unit cell volume starts to decrease once again. This is why the average volume of the unit cell reaches its maximum at about 35 min. In conclusion, the WAXS data is consistent with the remaining results, and also confirms the thesis on the two populations of crystallites originating during the isothermal crystallisation of ethylene-1-octene homogeneous copolymers. □

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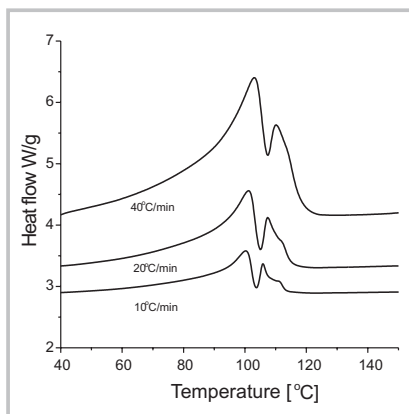


Figure 6. DSC scans for heating from 25°C to 150°C after isothermal crystallisation 102°C for 30 min. recorded with different heating rates (indicated in the Figure)

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**Bogumił Świdorski Ph. D.**  
Instytut  
Techniki i Technologii Dziewiarskich  
„TRICOTEXTIL”  
Institute of Knitting  
Techniques and Technologies  
ul. Piotrkowska 270,  
90-361 Łódź, Poland  
Phone: (48-42) 684-02-81,  
684-02-24, 681-02-11  
e-mail: office@tricotextil.lodz.pl