

REVERSED ANNEALING OF THERMAL FRACTIONATED POLYETHYLENES BY TMDSC

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Abstract

Polyethylene samples prepared by thermal fractionation (TF) were annealed in several consecutive cycles in a temperature modulated DSC (TMDSC) at a temperatures one °C below the peak temperatures, increased from cycle to cycle relative to these peaks. The transition enthalpy of each cooling cycle was greater or equal to that of the preceding heating cycle. The total heat-flows of each heating cycle corresponded to those of the samples in the reference state up until the vicinity of the annealing temperature. During the annealing, the heat capacities decreased to a lower value over a one minute period. The thermal memory effect caused by the thermal fractionation was eliminated by a small overheating of the material for a short time. The fast disappearance of the thermal memory by a relatively very small degree of heating above their melting temperature denies a long range physical separation of macromolecules by TF.

Keywords: annealing, crystallization, heat capacity, polyethylene, TMDSC, total heat-flow

Introduction

Thermal fractionation (TF) is a tool proposed to obtain information about the distribution of chain branching e.g. in polyethylenes (PE) [1–4]. The concept is based on Varga's work in 1986 [5, 6]. Accordingly the material is crystallised during consecutive isothermal periods carried out by stepwise cooling temperatures. The heat-flow curve, which was originally a smooth curve, is transformed into a multiple peak curve at the stepwise crystallised material. The phenomenon was called thermal memory effect of the polymer [5], and was investigated in details. This effect was produced originally on low density polyethylene (LDPE).

Recently branched polymers other than LDPE have been fractionated according to the density and the distribution of the branching within the macromolecules and the thermal behaviour of the fractionated materials has been studied by DSC [1–4]. The individual fractions showed different melting peak temperatures and from these fractions the melting of the non-fractionated material could be reconstructed by a

weighted summation [1, 2]. Similarly, the melting endotherm of a blend formed from different types of polyethylenes could be 'reconstructed' from its components [3]. The same technique was used to study the crystallisation of blends or modified polymers and called as Successive Self-Nucleation/Annealing by Müller *et al.* [7, 8].

In our previous studies [9–11], according to the expectations, we found that no TF effect could be observed for non-branched polymers like polypropylene (PP) or high density polyethylene (HDPE). We also did not expect TF for LLDPE prepared by metallocene catalysts (Me-LLDPE) as these polymers are supposed to be highly homogeneous and therefore fractions with different density of branching might not be present [9]. However, we obtained multiple peaks after the TF of Me-LLDPE samples by temperature modulated DSC (TMDSC) [11]. This result challenged the concept of TF or the concept of Me-LLDPE being highly homogeneous.

In our other research, the thermal behaviour of annealed semicrystalline polymers and their blends has been studied with TMDSC [12, 13]. The materials were annealed at temperatures just below their melting peak temperatures and the heat capacities were recorded during the annealing process which lasted for 10 min. The heat capacities decreased dramatically during the annealing both for the pure polymers [12] and for their blends (blends of PP with LLDPE) [13]. The change in the heat capacities was complete within 1–3 min. It was a very fast relaxation process. We have concluded from these experiments, that the reversible portion of the melting processes (i.e. heat-flow related to the heat capacities) can be attributed to the melting of the lamellar crystals connected by molecular chains. This concept is in harmony with Mathot's results, i.e. there is different crystallinity at different region of quenched LLDPEs [14], what means the bulk of a polymer melt is structurally inhomogeneous. This can also be related to the two-phase nature of the liquid LLDPE reported in [15].

This paper presents results using a special annealing process carried out on thermally fractionated PE materials in several consecutive heating and cooling cycles. The first 10-minute long annealing period was started 1 K below the lowest peak temperature of the TF material following a heating by $2^{\circ}\text{C min}^{-1}$ rate. After the annealing period the sample was cooled to 0°C by a $2^{\circ}\text{C min}^{-1}$ cooling rate. The annealing process was sequentially conducted for each subsequent melting peak in increasing order of temperature found in the TF samples by a preliminary TMDSC run carried out on the parallel sample. This was the reverse process of stepwise crystallisation, hence the name: reversed annealing.

Each of the heating runs was an analysing run for the effect caused by the preceding heating/cooling runs and an annealing cycle for the following melting run.

Experimental

Materials

The type, the density and the melt flow index of the materials used in this work are summarised in Table 1.

Table 1 The type, the density and the melt flow index of the materials

Material	Polymerised	Comonomer	Density/kg m ⁻³	MFI/g 10 min ⁻¹ *
C8-LLDPE1	in solution	octene	923	0.94
C8-LLDPE2	in solution	octene	923	1.10
C6-LLDPE	in gas phase	hexane	922	0.78
C4-LLDPE	in gas phase	butene	918	1.00
Me-LLDPE	by metallocene	butene	910	1.20
HDPE	Ziegler-Natta	–	NA	0.20

*MFI was determined at 190°C using 2.6 kg load according to ASTM D1238

Methods

Sample preparation (thermal fractionation)

5–10 mg of flat samples have been placed in a TA Instruments TMDSC pan covered by a lid and two parallel (in reference and sample sensors) samples were heated to 150°C in a Perkin-Elmer DSC7. The samples were crystallised by step-wise cooling according to the cycles shown in Table 2. Following the jump to the crystallisation temperature, isothermal conditions were applied for 100 min. A total of 8 cooling steps were used for each material. After the last crystallisation isotherm, the samples were cooled to room temperature at a natural cooling rate.

Table 2 Temperatures of the isothermal crystallisation and the annealing (°C)

Cycles	1	2	3	4	5	6	7	8	Melting
Crystallisation isotherms									
HDPE	136	132	128	124	120	116	112	108	–
LLDPE	122	118	114	110	106	102	98	94	–
Me-LLDPE	94	90	86	82	78	74	70	66	–
Annealing isotherms									
HDPE	100	104	108	112	116	121	126	131	150
LLDPE	99	103	107	111	115	120	125	–	150
Me-LLDPE	64	68	72	76	80	84	88	92	125

TMDSC

TA Instruments TMDSC has been used to perform the reversed annealing with the cell connected to an intercooler. 2°C min⁻¹ heating and cooling rates were applied with 40 sec as sinusoidal modulation period and 0.6°C as modulation amplitude. This was a modulation with a medium depth [10].

The TF samples have been analysed prior to this work in a TMDSC to get the information about the peak temperatures. The results are given in our previous paper [11].

Reversed annealing

Samples prepared parallel with the ones used to determine the basic thermal behaviour of TF materials, were heated to the temperatures 1°C below the peak temperature of its first endothermic peak (heating run). They were kept at this temperature for 10 min (annealing) then cooled to 0°C by 2°C min⁻¹ cooling rate (cooling run). This heating/annealing/cooling cycle was repeated sequentially for each peak (or shoulder) that had been detected in the TF samples by the preliminary TMDSC run. The annealing temperatures of the consecutive cycles for the investigated materials are shown in Table 2.

Final test

After the last annealing cycle the samples were heated to 20–30°C above their melting temperatures in two additional cycles. The aim of these cycles was to test the effect of the reversed annealing process on the melting process (1st melting cycle). It was also the aim to check the degree of the damage caused by the long time heat treatment (2nd melting cycle, i.e. heating and cooling cycles from a standard state).

The total heat-flow and the heat capacity were recorded as primary data, the reversing and the kinetic heat-flows were calculated from them. Only the total heat-flow and the heat capacity curves are shown in this paper. Endothermic heat-flow is shown upwards in the Figures.

The total heat-flows have been integrated both in the heating and in the cooling runs of each consecutive annealing step. As the heat-flow curves before the changes were identical, the same baseline determined from the last two melting cycles was used in the integration. The calculations were carried out within the interpreting software of Microcal Origin in each case.

Results

Figures 1 and 2 show the total heat-flow obtained for C8-LLDPE1 in the consecutive annealing and melting cycles. Figure 1 shows the curves obtained in the heating cycles and those obtained on cooling are shown in Fig. 2. The data has been offset on the heat-flow axes for clarity.

The total heat-flow of each heating cycle follows that for the non-fractionated material in a standard state up to 70°C. The first heating run has higher heat-flow values above this temperature, then there is a maximum. This is followed by a minimum, then a second maximum is observed at the point where the increase in the temperature was stopped. The next heating runs follow that of the standard cycle near to the temperature of annealing and they do not have maxima at the same temperatures as the preceding ones. They have a minimum at the annealing temperatures. This means heating the TF sample by no more than 2°C over its peak temperature eliminates the thermal memory from the sample. The annealing shifts the melting peak temperature to a higher one. This phenomenon was also observed in our previous work [13].

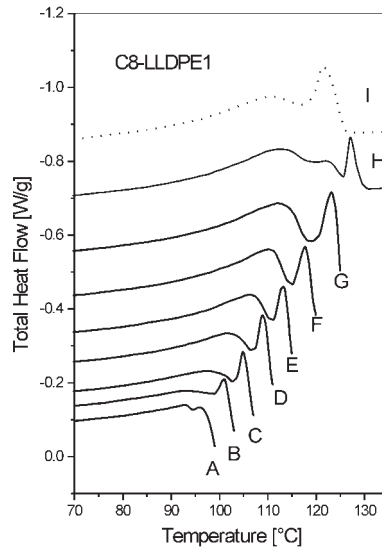


Fig. 1 Total heat-flow of C8-LLDPE1 upon heating during consecutive annealing cycles. A–G: annealing at 99, 103, 107, 111, 115, 120 and 125°C respectively, H and I: first and second melting cycles after annealing cycles. Endotherm upwards

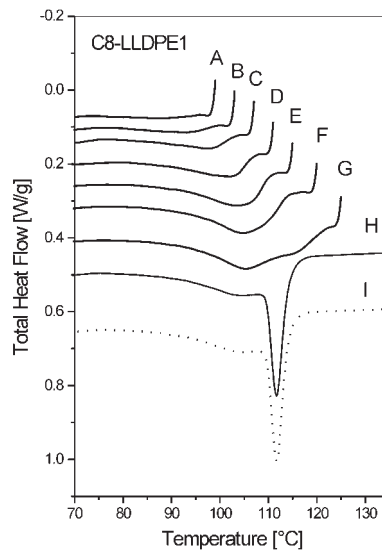


Fig. 2 Total heat flow of C8-LLDPE1 upon cooling during consecutive annealing cycles. A–G: annealing at 99, 103, 107, 111, 115, 120 and 125°C respectively, H and I: first and second melting cycles after annealing cycles. Exotherm downwards

The heat-flows upon cooling have a small maximum just after the annealing temperature then the heat-flow increases to the level of the cooling run in a non-fractionated standard state. There is an exothermic heat-flow upon cooling. This corresponds to our previous observation on semi-crystalline materials annealed near to their melting temperature [13].

Figure 3 shows the heat capacities of C8-LLDPE1 in all of the consecutive cycles. Here heat capacities measured both in the heating and in the cooling runs have been compared. The data have been offset on the heat flow axis for clarity. Figure 4 directly compares the heat capacities of the heating cycles alone.

The first heating cycle starts with higher heat capacities up to the annealing temperature with respect to the standard state. Then it decreases to the value of the already crystallised material. The next cycle results in heat capacities according to those of the standard cycle up to 83°C, then they decline forming a minimum at the temperature corresponding to that of the previous annealing. A maximum is formed after the minimum due to stopping the heating and starting the annealing. Each further heating cycle behaves similarly. They have a minimum at the annealing temperature of the preceding cycle followed by a maximum. After the maximum the heat capacities decreased to the value of the following cooling run. The maxima are below the heat capacities of the standard cycle at the same temperature, with the exception of the first melting cycle where annealing shifts the heat capacities to higher temperatures by approximately 5°C.

The heat capacities upon cooling decrease in the first cycles. They show then a broad maximum and follow an extrapolated higher value when the annealing temper-

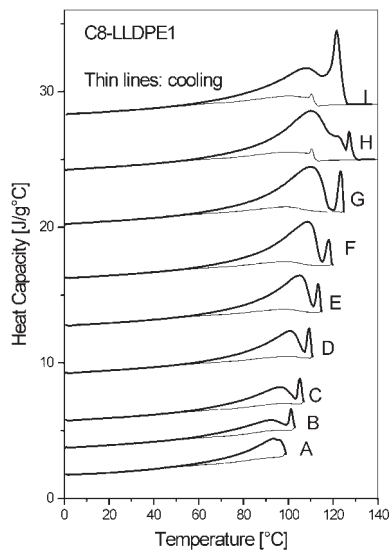


Fig. 3 Heat capacities of C8-LLDPE1 during consecutive annealing cycles. A–G: at 99, 103, 107, 111, 115, 120 and 125°C respectively, H and I: first and second melting cycles after annealing cycles

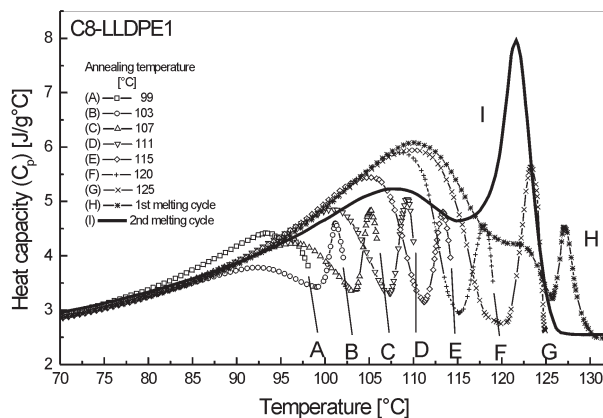


Fig. 4 Heat capacities of C8-LLDPE1 upon heating during consecutive annealing cycles. A–G: annealing at 99, 103, 107, 111, 115, 120 and 125°C respectively, H and I: first and second melting cycles after annealing cycles

ature was higher than the temperature of crystallisation of the melt at $2^{\circ}\text{C min}^{-1}$ cooling rate. This means, the partly crystalline material within the melt has higher heat capacities than the melt itself.

The first melting curve shows a higher heat capacity from 70°C than that of the standard material. The effect is not seen during the following heating cycles. The comparison of the heat capacities above 90°C upon heating, however, shows that they form a universal curve and are also higher than those of the standard crystallised material (Fig. 4, curves B–G).

The curves for C8-LLDPE2, C6-LLDPE and C6-LLDPE are similar to those of C8-LLDPE1. They are not given here but they can be obtained from the authors on request. The behaviour of C8-LLDPE2 is very much similar to those of C8-LLDPE1. The only basic difference is that the heat capacities in the heating cycles correspond to those of the standard cycle, where there is no increase in the heat capacities.

Similar data were found for the C6-LLDPE. This material has much lower heat-flow and heat capacity values before the melting temperature and both curves are dominated by the melting peak itself. The heat capacities upon cooling do not show a broad maximum and the last peak has a much higher value than those of the previous materials. The heat capacities in the heating cycles do not exceed those of the standard cycle with the exception of the first one.

C4-LLDPE behaves in many respects similar to C8-LLDPE2.

Figures 5–8 show the same data for Me-LLDPE. The effect of the reversed annealing on this material is small, particularly at temperatures as low as $64\text{--}80^{\circ}\text{C}$. (The total heat-flow of the first annealing cycle is not shown in Figs 5 and 6.) There is only a very small peak in the total heat-flows, the peak increased only when the annealing was within the temperature range of the melting peak. The heat capacities upon cooling do not differ markedly from those of the heating cycles. They are smaller than

those of the standard state material in the first annealing cycle up to the annealing temperature of 84°C, then they follow the heat capacity curve of the standard state material. A sharp peak is observed in the heat capacities at the first melting cycle but this peak is not shifted to higher temperature as was the case with the other LLDPEs.

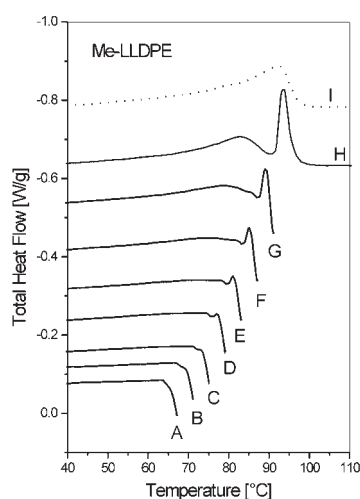


Fig. 5 Total heat flow of Me-LLDPE upon heating during consecutive annealing cycles. A–G: annealing at 68, 72, 76, 80, 84, 88 and 92°C respectively, H and I: first and second melting cycles after annealing cycles. Endotherm upwards

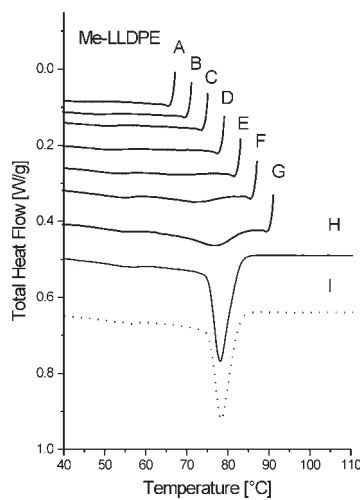


Fig. 6 Total heat flow of Me-LLDPE upon cooling during consecutive annealing cycles. A–G: annealing at 68, 72, 76, 80, 84, 88 and 92°C respectively, H and I: first and second melting cycles after annealing cycles. Exotherm downwards

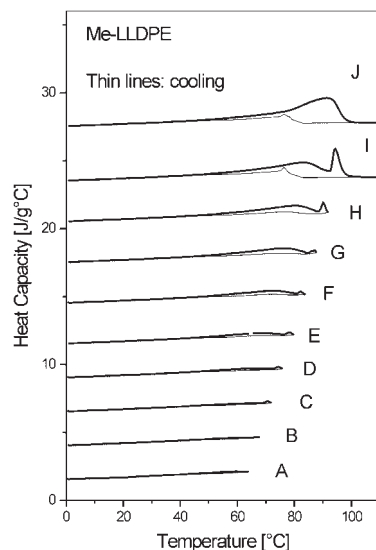


Fig. 7 Heat capacities of Me-LLDPE during consecutive annealing cycles. A–H: annealing at 64, 68, 72, 76, 80, 84, 88 and 92°C respectively, I and J: first and second melting cycles after annealing cycles

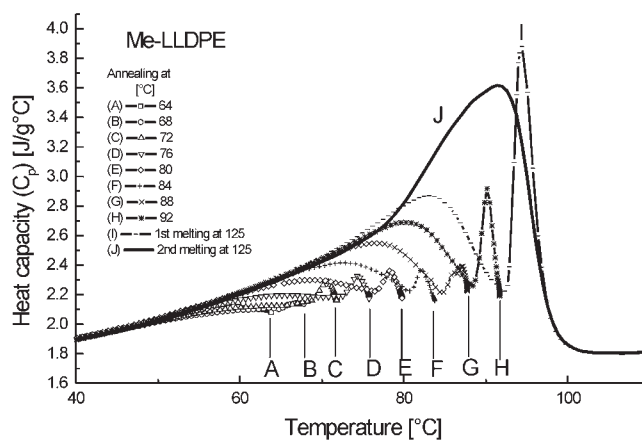


Fig. 8 Heat capacities of Me-LLDPE upon heating during consecutive annealing cycles. A–H: annealing at 64, 68, 72, 76, 80, 84, 88 and 92°C respectively, I and J: first and second melting cycles after annealing cycles

Figures 9–12 show the results for HDPE. There was no peak formation by the TF process, therefore we did not expect any considerable effect of the reversed annealing of this material. The Figures show the opposite. The effect here is much smaller than the ef-

fect for LLDPEs, but they can be compared with those of Me-LLDPE. There is a local minimum in the heat-flow curves at the annealing temperatures, then a maximum is observed. There is a small maximum in the total heat flow curves upon cooling when the cooling is started. An additional broad maximum can be seen in Fig. 9 at cycle F in the temperature ranges corresponding to the crystallisation from the melt G and H.

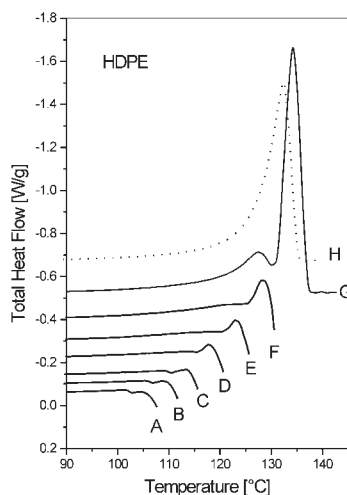


Fig. 9 Total heat flow of HDPE upon heating during consecutive annealing cycles. A–F: annealing at 108, 112, 116, 121, 126 and 131°C respectively, G and H: first and second melting cycles after annealing cycles. Exotherm upwards

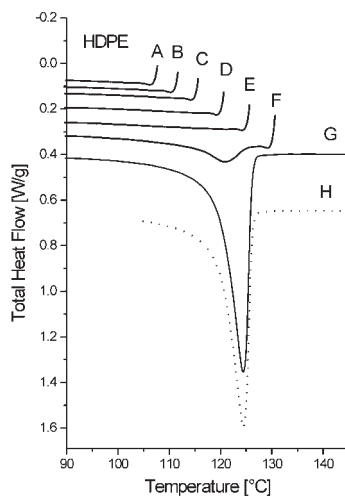


Fig. 10 Total heat flow of HDPE upon cooling during consecutive annealing cycles. A–F: annealing at 108, 112, 116, 121, 126 and 131°C respectively, G and H: first and second melting cycles after annealing cycles. Exotherm downwards

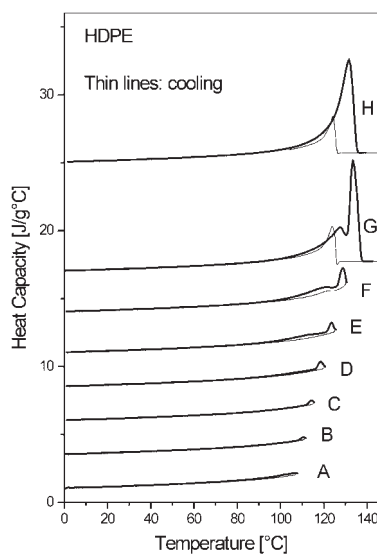


Fig. 11 Heat capacities of HDPE during consecutive annealing cycles. A–F: annealing 108, 112, 116, 121, 126 and 131°C respectively, G and H: first and second melting cycles after annealing cycles

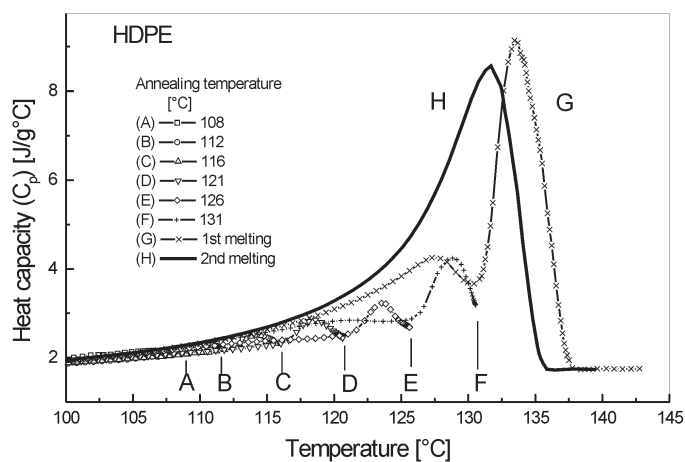


Fig. 12 Heat capacities of HDPE upon heating during consecutive annealing cycles. A–F: annealing at 108, 112, 116, 121, 126 and 131°C respectively, G and H: first and second melting cycles after annealing cycles

The heat capacities show small, but increasing peaks before the annealing above 110°C (curves B–F). The heat capacities are below those of the standard cycle. The greatest difference can be seen after the last annealing cycle. There is a shift of the

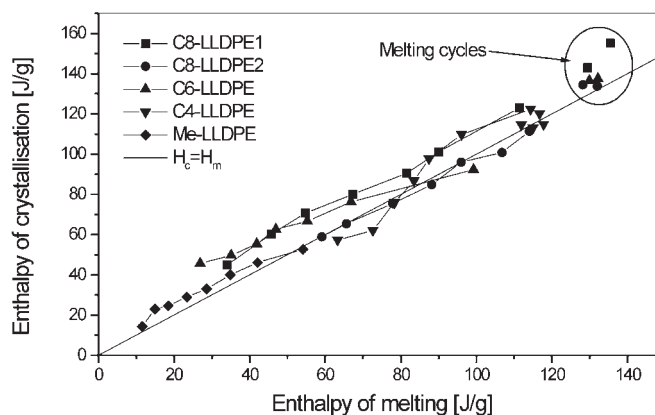


Fig. 13 Enthalpy of crystallisation vs. enthalpy of melting of each individual annealing and melting cycles for the different polyethylenes

heat capacities toward higher temperatures and the annealing resulted in a great loss in the heat capacities below the melting temperature. The heat capacity values are shifted to higher temperatures by 3–4°C.

Figure 13 compares the transition enthalpies integrated in cooling runs as the function of those of the heating runs. There is a linear relationship between the heating and the cooling data. The enthalpies upon cooling are generally higher than those upon heating. It refers to a further melting during the annealing period, when the temperature slightly shifted to higher values. The effect of the temperature shift could not be taken into consideration during the integration of the transition enthalpies. The results show undoubtedly, that the recrystallisation does not occur during the annealing periods, it is the result of the cooling.

Discussion

The annealing experiment has been performed for LLDPEs in a temperature range where the heat capacities measured on heating are different from those measured upon cooling. This is the temperature range, which has been considered as a transition region for semi-crystalline polymers in our previous research [17]. This range started nearly at 50°C for the other LLDPEs including Me-LLDPE, but at 110°C for HDPE. The annealing of HDPE started below this temperature. HDPE could not be thermally fractionated as had been expected, but against expectations, Me-LLDPE could be fractionated.

Reversed annealing showed a very rapid disappearance of the effect of the thermal fractionation and at a very small degree of heating over the fractionation peak temperature. If we suppose that this was really a fractionation, i.e. a separation of macromolecules according to their branching densities, this fast and low energy-driven relaxation to the original state would not be expected, it is surprising.

The reversed annealing influenced the heat capacities upon heating, i.e. the reversible transitions of the system. Thermal fractionation reduced the reversibility of the melting as has been previously shown [10, 11]. The reversed annealing restores the reversibility. There is some transformation of the heat capacities from one temperature to another, but the integral of the reversing heat-flow over the transition range did not change during the 1st melting cycles. Rather, they resulted in the same value as for the second cycles for each material. This means, the overall reversibility did not change after reversed annealing.

There is a shift in the peak position for each annealing cycle indicating that the annealing itself increased the melting temperature of the affected fraction. The greatest and unequivocal effect is visible after the last melting peak. The only exception is with the Me-LLDPE where there is no shift in the melting peak at the highest temperatures. This shows a normal annealing effect.

The data shown above do not support the concept of a thermal fractionation. A fractionation according to branching cannot be recovered in such a short time at a temperature so close to the melting temperature of the individual fractions. The phenomenon can rather be explained by an annealing of the amorphous phase, which is connected to the crystalline phase by tie molecules as has been proposed in [12]. This approach is also supported by the conclusion given by Kavesh and Schultz [18], that above the crystallisation temperature melting and recrystallisation occur due to the interaction of the crystalline lamellae and the connected chains being in the amorphous phase. In this experiment we could see that this recrystallisation occurs during the cooling run of the cycle and not during the time when the sample was kept at a constant temperature, at the maximal temperature of the cycle (annealing). Therefore, it seems to us that the annealing effects the amorphous phase connected to the crystalline one, and the recrystallisation is a realization of the changes in the structure of the amorphous phase in the cooling run.

Conclusions

Reverse annealing experiments challenge the concept of thermal fractionation caused by step-wise crystallisation. The fast disappearance of the thermal memory by a relatively very small degree of heating above their melting temperature denies a long range physical separation of macromolecules according to their branching characteristics. It can concern only parts of the molecules.

An increase in the melting peak temperature by the reversed annealing might be related to an increase in the lamellar thickness of the crystalline phase. We hope that this change might be studied by X-ray diffraction techniques. Further structural studies should be carried out to show the nature of the changes in the structure of the semicrystalline systems caused by the reversed annealing process.

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