Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

REVERSIBLE MELTING OF SEMI-CRYSTALLINE POLYMERS
2. Annealing near to the melting point

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Abstract

Annealing experiments have been carried out at a few degrees below the melting point of different polyethylenes (LDPE, LLDPE, HDPE), of polypropylene (PP) and of Nylon-6. The heat capacities decrease during the annealing, within a 2–4 min time scale, to a lower value which corresponds to the extrapolated heat capacity values obtained for the cooling cycle when the polymer is cooled from the melt. Heat capacities in the heating cycle following the cooling cycle of PP, Nylon-6 and HDPE have the same value as during the cooling section. This is not the case for LDPE and LLDPE.

Exothermic total heat flow in the cooling section following the annealing indicates that the crystallisation takes place during the cooling rather than during the annealing period. The total melting enthalpy measured before and after the annealing cycle is the same.

The reversing heat flow shows an excellent fit to the change of the crystallinity measured by small angle scattering of synchrotron radiation during a heating cycle at temperatures below the melting peak.

A coupled thermodynamic interaction of the crystalline and the amorphous phases is concluded from this study. This kind of interaction is possible at the lateral end of polymeric chains incorporated into the crystalline phase. This is an indication of the portion of tie molecules in the system, i.e. the portion of fringed micelle type of crystalline morphology with respect to that of folded chain lamellae.

Keywords: crystallisation, fringed micelle, heat capacity, MDSC, melting, semi-crystalline polymers

Introduction

In our previous paper [1] we have showed that MDSC (produced by TA Instruments) results in reproducible recordings of the heat capacities and the total heat flow of semi-crystalline polymers. It has also been shown [1] that the heat

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capacity signal produced by the hardware depends on the modulation frequency and this dependence is universal, that is, it does not depend on the material being studied. Therefore the heat capacities measured at a given modulation period (p), can be recalculated to those of the hypothetical zero frequency. It has also been concluded in another paper [2], that the heat capacity of the semi-crystalline polymers at their melting range also depends on the frequency: with decreasing modulation period the reversing (heat capacity) component of the melting enthalpy decreases. There is a lower limit of this value with decreasing modulation time, i.e. there is always a reversible component of the melting process. This limit depends on the type of the polymer, e.g. it is increasing in different types of polyethylene in the order: HDPE>LLDPE>VLDPE>LDPE [2, 3].

Wunderlich [4] compared the measured heat capacities to those calculated from molecular vibration theories and found discrepancies between the measured and the calculated values. The measured values showed some excess heat capacities above a given temperature depending on the polymer. Wunderlich suggested a mechanism to explain the existence of the excess heat capacities (so-called mesophase, or condis crystal) but this mechanism does not seem to be suitable to describe the temperature dependence as well as the relaxation character of this excess heat capacity [2]. In a recent paper Okazaki and Wunderlich [5] observed that the melting is reversible but they did not give explanation of the phenomenon.

MDSC makes it possible to record heat capacities while the underlying heating or cooling rate is zero, i.e. during annealing at constant temperature (with a small oscillation in the temperature e.g. less than 0.6 K). Upon annealing (or cooling after heating below the melting point) the crystalline particles as nuclei are already present in the system. This means, primary nucleation process [6, 7] are not necessary for the crystallisation. When the melting process is stopped at a given temperature and the melt is started to be cooled in the presence of polymeric crystals the crystalline growth process will determine the nature of the response. The growth process in the folded chain lamellar model is controlled by additional nucleation called secondary ad tertiary nucleation processes. Secondary nucleation is necessary to form a new layer on a crystal surface, tertiary nucleation is necessary to add a new molecular segment to the crystalline surface. Both needs supercooling according to the recent concepts [6]. Accordingly the change in the crystallinity during annealing can not be reversible.

In this paper we present data obtained on the annealing of some semi-crystalline homopolymers. We try to find a reasonable explanation of this excess heat capacity during the melting process.

Experimental

Experimental method

A TA Instruments MDSC was used in this study. All of the cycles have been performed by $\beta=2$ K min^{-1} heating and cooling rates using $p=40$ s modulation

period and 0.6 K modulation amplitude. In order to eliminate the thermal history of the samples a preliminary cycle involving melting and recrystallisation has been carried out (standardising cycle). The standardising cycle was followed by the first cycle where data was collected and this is called standard cycle in the Figures.

Table 1 Melting enthalpies in the standard and in the analysing of different polymers

$\Delta H / J \ g^{-1}$	PP	Nylon-6	HDPE	LLDPE	LDPE1	LDPE2
Standard cycle, heating						
Total	126.5	143.5	216.9	112.9	93.6	55.7
Reversing	72.9	63.2	133.0	83.9	90.2	57.0
Kinetic	51.4	79.0	80.5	28.9	3.3	−1.3
Standard cycle, cooling						
Total	−117.4	79.0	−216.5	−116.0	−92.4	−59.6
Analysing cycle, heating						
Total	145.5	88.4	223.0	113.4	91.6	55.1
Reversing	43.9	55.0	128.9	81.1	81.3	52.8
Kinetic	101.0	32.8	91.5	34.6	12.4	3.2
Analysing cycle, cooling						
Total	−120.0	−8.2	−202.3	−114.1	−91.1	−59.2
Reversing	−2.4	−12.6	−27.4	−20.6	−21.2	−14.9
Kinetic	−116.7	−85.2	−178.0	−94.7	−65.6	−45.6

The annealing experiments were carried out as follows: after a standard cycle the temperature was raised 3–5°C below the melting point (peak temperature, determined in a previous experiment) and the system was annealed for 10 min. Then the sample was cooled to 40°C to terminate the annealing cycle. The following cycle was an analysing cycle for the system which was annealed by the previous heating cycle. A supplementary heating/cooling cycle (a second analysis equivalent to a standard cycle) of the polymers showed that the system did not change, it is in the standard state since the DSC curves were exactly the same as those of the reference state (shown in the standard cycle). The DSC curves of the standardising and second analysing cycles are not shown in the Figures. The melting enthalpy of the standard as well as of the analysing cycles are collected in Table 1.

Materials and sample preparation

The following materials have been used for the study:

HDPE	HDX953, Kemcor product, an injection moulding grade polymer, MFI: 30 g 10 min⁻¹.

HDPE HDX953, Kemcor product, an injection moulding grade polymer, MFI: 30 g 10 min^{-1}.

LLDPE ET6013, ICI product, an injection moulding grade polymer, MFI: 1 g 10 min^{-1}. Density: 922 kg m^{-3}.

LDPE1 WNC176, ICI product, an extra coating grade polyethylene, MFI: 7.6 g 10 min^{-1}. Density: 919 kg m^{-3}.

LDPE2 XHF179, ICI product, a blow film grade polyethylene, MFI: 1.0 g 10 min^{-1}. Density: 921 kg m^{-3}.

PP ICI GWM22 injection mould grade polymer, MFI: 4 g 10 min^{-1}.

Nylon 6 BASF Ultramid 6, an injection moulding grade polymer, MFI: 70 g 10 min^{-1}.

All the samples have been cut from injection moulded test bars. Further details of the experimental conditions are given in our previous papers [1, 2].

Results

Annealing near to the melting temperature

Figure 1 shows the heat capacities of PP during the standardisg and standard cycles respectively. The first cycle shows a broader transition peak than the second one. The difference in the heat capacities between the cycles reflect the thermal history of the PP (injection moulding in this case). A broad shoulder and a sharp peak just below the melting temperature are characteristic of this type of PP in the standard state. A temperature just below the second sharp peak was selected for the annealing experiments.
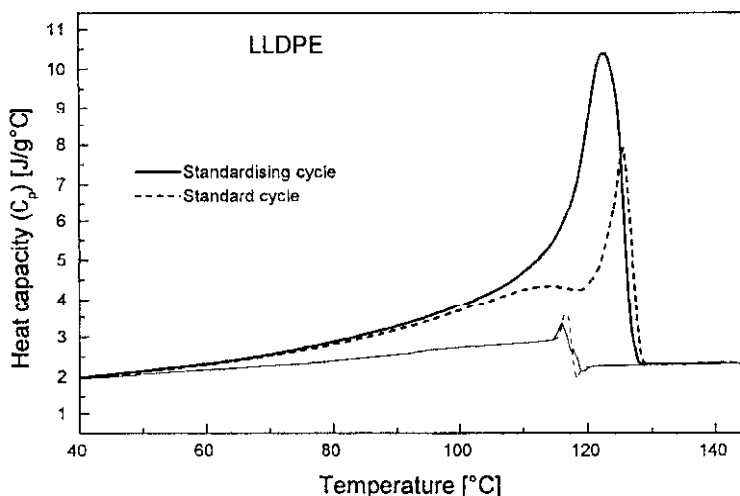

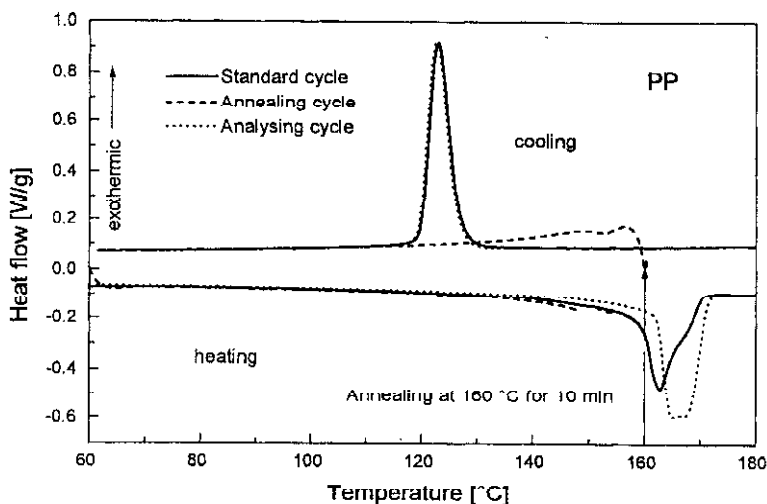Fig. 1 Heat capacities of PP in the standardising and standard cycles

Fig. 2 Total heat flow of PP before, during and after being annealed at 160°C for 10 min

The total heat flows during the standard, the annealing and the analysing cycles of PP are shown in Fig. 2. The annealing experiment has been carried out here in two steps. First the sample has been heated by $\beta=5$ K min^{-1} up to 145°C (the heat flow is recalculated to that of $\beta=2$ K min^{-1}) then the heating was continued by $\beta=2$ K min^{-1} and stopped at 160°C, where the sample was kept for 10 min. A cooling by $\beta=2$ K min^{-1} down to 70°C followed the annealing then an analysing cycle showed the results of the annealing.

The total heat flow in the annealing cycle was the same as in the standard cycle up to the annealing temperature. An endothermic transition has already begun before the annealing. The total heat flow is exothermic upon cooling and it is a mirror of the total heat flow shown by heating. The total transition enthalpy value in the second analysing cycle was the same as that in the first one (Table 1) the amount of crystallinity did not change during the annealing experiment . This means the crystallisation occurred during the cooling cycle and not when the material was annealed. Nevertheless the transition enthalpy of the reversing heat flow is lower in the analysing cycle than it was in the standardising one.

Figure 3 shows the heat capacities during the same cycles shown on Fig. 2. The heat capacities on the annealing cycle are higher than on the standard cycle then they decrease during the annealing to a lower level. In the analysing cycle the heat capacities did not follow those of the standard cycle, they followed the heat capacities produced by the annealing. A sharp and more intense peak developed above the annealing temperature but the total area under the melting for the analysing cycle was only slightly less than the area under the melting peak in the standard cycle.
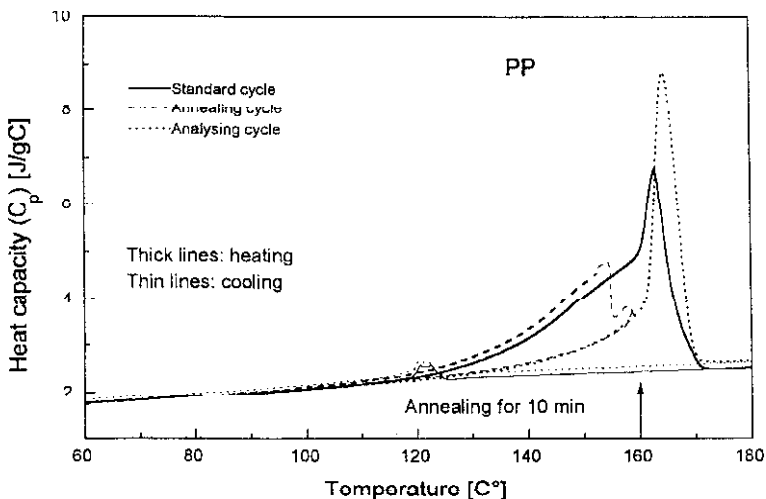
Fig. 3 Heat capacities of PP before, during and after being annealed at 160°C for 10 min
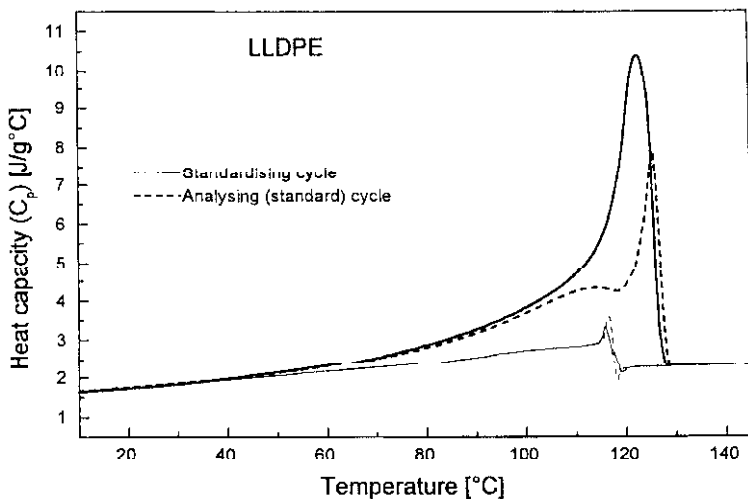

Fig. 4 Heat capacities of LLDPE in the standardising and standard cycles

Figure 4 shows the heat capacities during the standardising and the standard cycle of LLDPE. The heat capacities in the standard cycle follow those of the standardising cycle up to 90°C, than their values shows a broad peak at 110°C and a sharp one at 125°C. The annealing was carried out at the start of this second peak, i.e. at 121°C.

Figures 5 and 6 show the total heat flow thermogram and the heat capacities in the standard, annealing and analysing cycles for LLDPE. The total heat flow
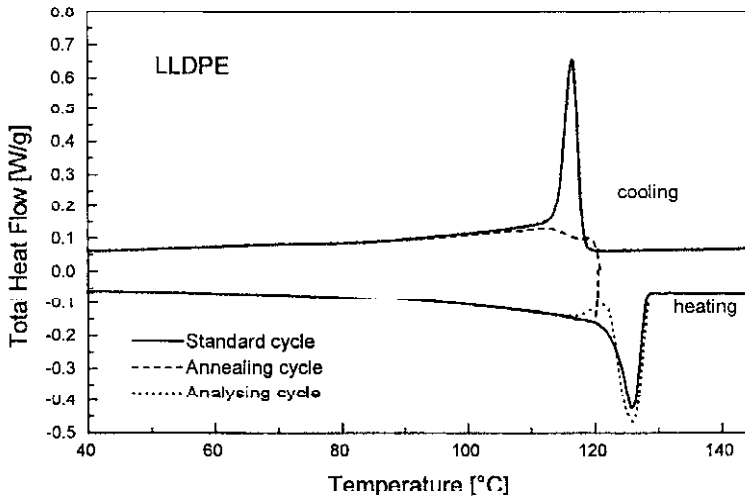
Fig. 5 Total heat flow of LLDPE before, during and after being annealed at 121°C for 10 min
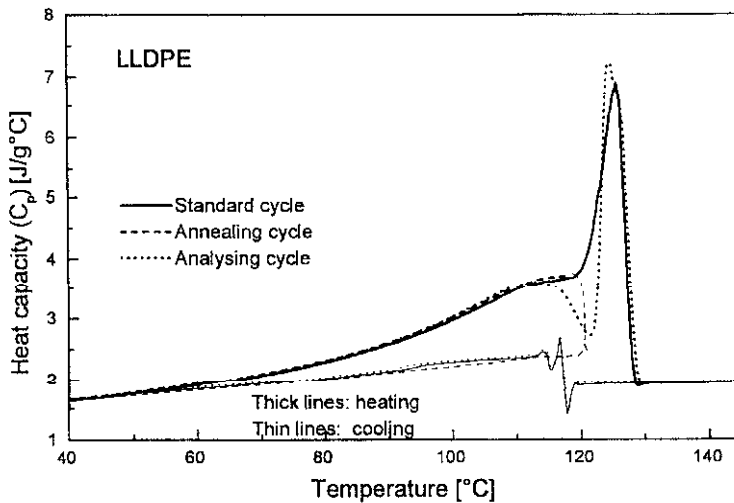

Fig. 6 Heat capacities of LLDPE before, during and after being annealed at 121°C for 10 min

in the annealing cycle was again the same as that of the standard cycle up to the annealing temperature. Upon cooling a definite exothermic peak is present on the heat flow below the crystallisation temperature of LLDPE (<115°C). The analysing cycle shows a decrease in the heat flow near to the temperature of the annealing and this is followed by a melting peak sharper than in the standard cycle. The total melting heat integrated from 70°C to 130°C did not change during the annaeling process (Table 1).
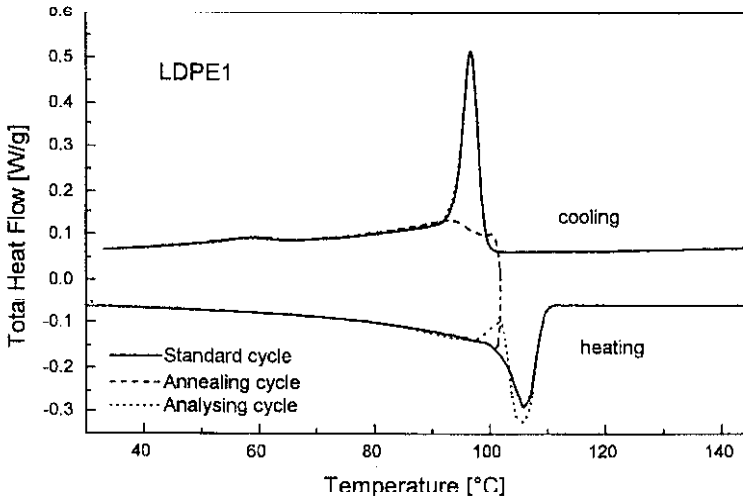
Fig. 7 Total heat flow of LDPE1 before, during and after being annealed at 107°C for 10 min
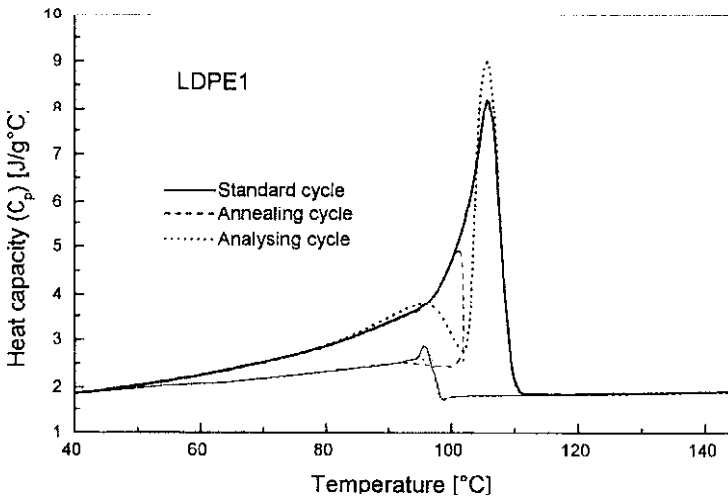

Fig. 8 Heat capacities of LDPE1 before, during and after being annealed at 107°C for 10 min

The heat capacities of the LLDPE (Fig. 6) decrease during the annealing to the value extrapolated from that of the already crystallised LLDPE. In the analysing cycle during heating, the heat capacities up to the annealing temperature were the same as those in the heating part of the standard cycle. This is a difference in the behaviour of LLDPE with respect to PP. There is a decrease in the heat capacities near the annealing temperature then a sharp peak follows. The transition enthalpy determined from the reversing heat flow in the annealing cycle decreased with respect to the standard cycle (Table 1).
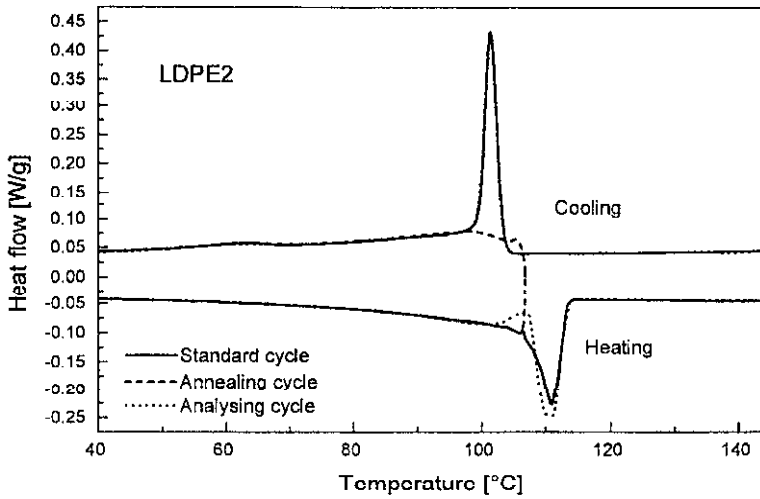
Fig. 9 Total heat flow of LDPE2 before, during and after being annealed at 101°C for 10 min
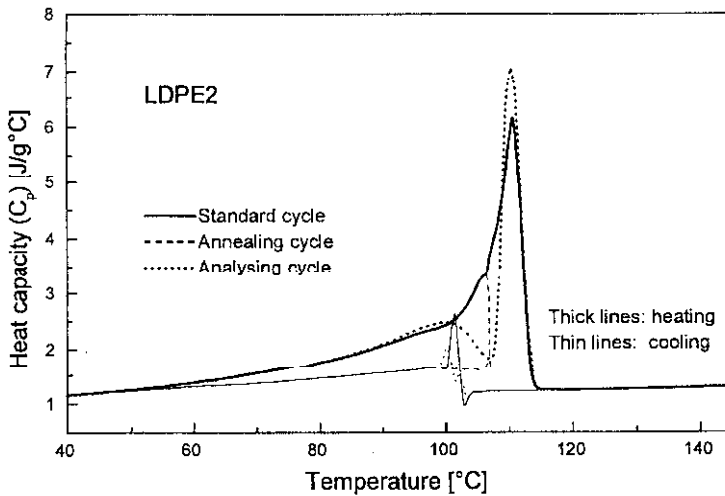

Fig. 10 Heat capacities of LDPE2 before, during and after being annealed at 101°C for 10 min

Figures 7 and 8 represent the data obtained for LDPE1 and Figs 9 and 10 show data for LDPE2. As the melting temperatures of the two LDPEs are different the annealing temperatures selected are different. LDPE1 was annealed at 107°C, and LDPE2 at 101°C.

Similar features to those observed for LLDPE can be seen on the Figures. The total enthalpies of melting and crystallisation are less than those of LLDPE. The
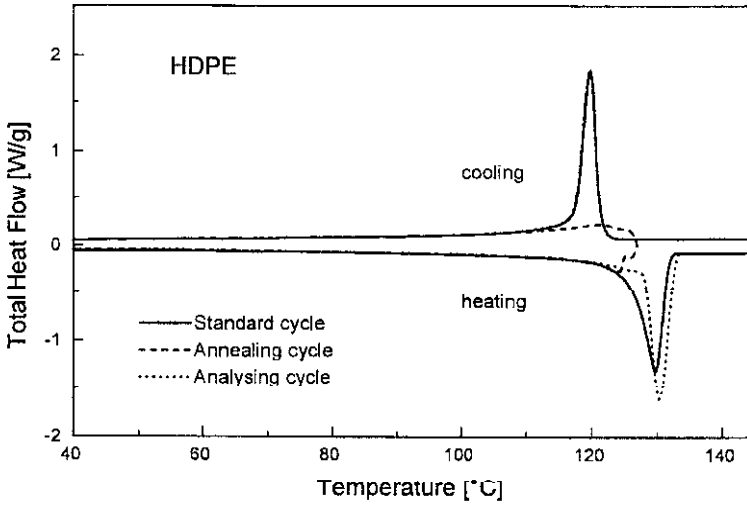
Fig. 11 Total heat flow of HDPE before, during and after being annealed at 127°C for 10 min
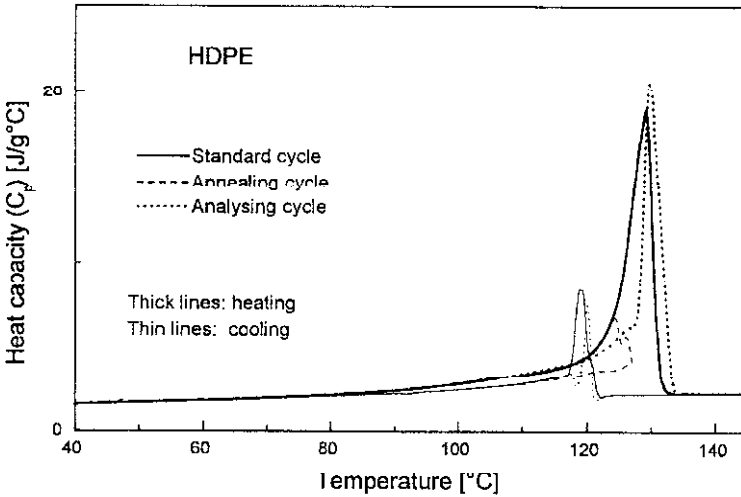

Fig. 12 Heat capacities of HDPE before, during and after being annealed at 127°C for 10 min

reversible part of the melting enthalpies are similar to those of the total enthalpies of melting and in one case it is greater. The melting of these polymers is nearly a completely reversing process. It is worth mentioning that on cooling there is a step in the reversing heat flow of all these PEs following the crystallisation (seen on the heat capacity charts). The area under this step is the reversing enthalpy of and it increases in its contribution to the total enthalpy with decreasing melting point of the PE.

Figures 11 and 12 are the total heat flow and the heat capacity charts of the HDPE during the annealing experiments.The characteristics of the charts are similar to those of PP but not LDPE or LLDPE. The reversing portion of transition enthalpy of crystallisation on cooling in both the standard and analysing cycles is the smallest portion of the total enthalpy with respect to all of the PE samples, nevertheless, its absolute value is the greatest.
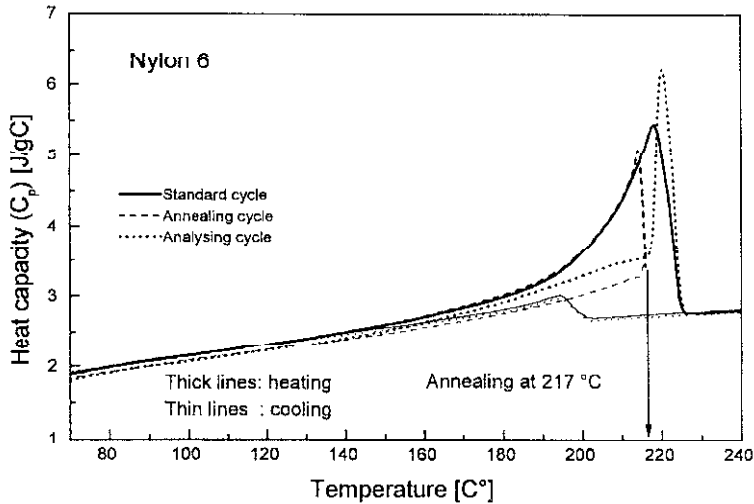

Fig. 13 Heat capacities of Nylon-6 before, during and after being annealed at 217°C for 10 min
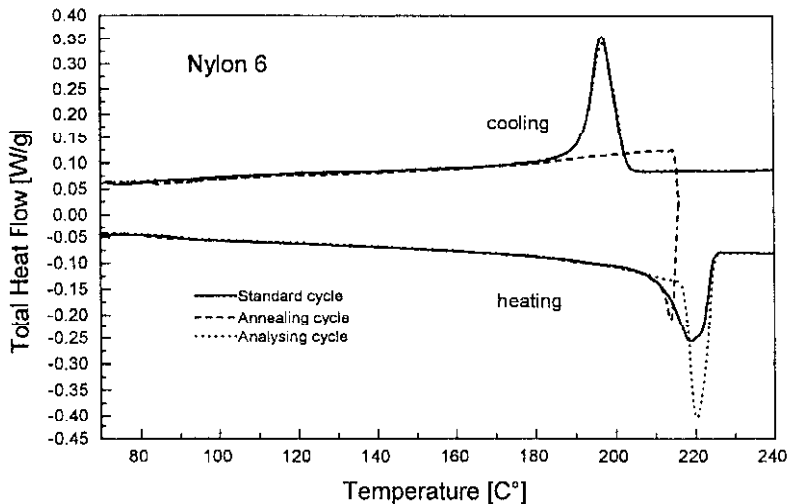

Fig. 14 Total heat flow of Nylon-6 before, during and after being annealed at 217°C for 10 min

Figures 13 and 14 show the heat capacity and total heat flow charts of Nylon-6 during an annealing experiment at 217°C. Nylon's behaviour is similar to that of LLDPE but not PP. This means, it has higher heat capacities after being cooled from the temperature of annealing and heated again.
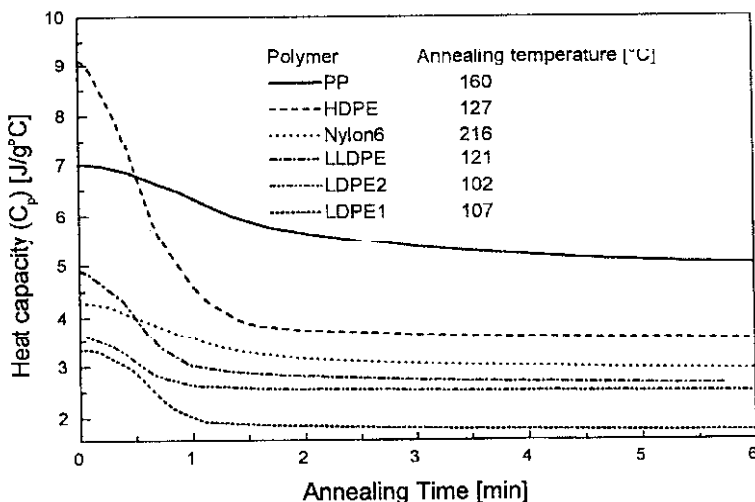

Fig. 15 Change of the heat capacities of the different PE, PP and of Nylon-6 by the annealing time

Figure 15 shows the change of the heat capacities during the annealing period for the investigated polymers. The heat capacities fall rapidly (in 1–3 min) to their smaller values. These values were reproduced by the analysing cycle upon heating at PP, HDPE and Nylon-6. The heat capacities then increase sharply to a greater value than they were before the annealing forming a transition peak.

Camparison to the crystallinity

We do not have useful crystallinity *vs.* temperature data to be able to compare the thermometric charts to the chart of crystallinity *vs.* temperature. Forgacs *et al.* [8] compared qualitatively the crystallinity data to the calorimetric data using synchrotron radiation and density measurements for measuring the crystallinity during the melting process. The change in the crystallinity calculated from the wide angle X-ray scattering intensities could have been compared to the heat flow chart.

Recently crystallographic data of HDPE as a function of the temperature are available from Ryan [9]. He did not give details of the grade of the HDPE he used in his experiments. According to a personal communication, the material was an extrusion grade HDPE. We can compare his data to the measured thermometric charts shown in our previous work [2, 3].
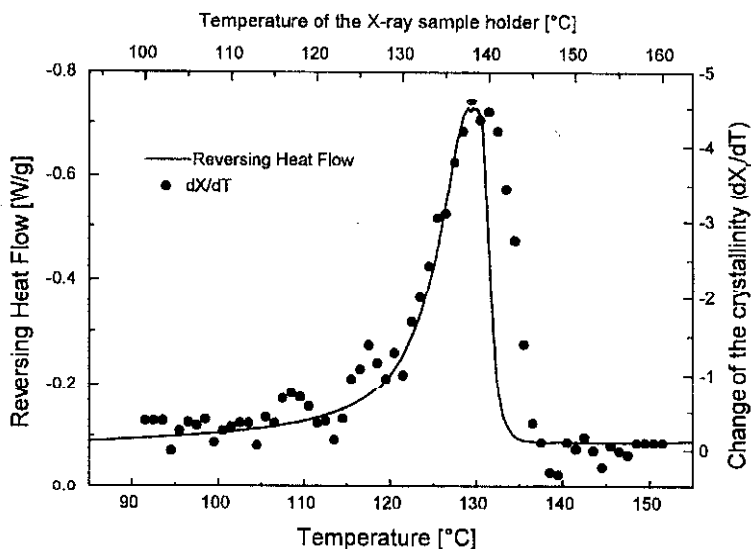
Fig. 16 Comparison of the change of crystallinity of HDPE with that of the heat capacities by the temperature

Figure 16 compares the reversing heat flow of HDPE (continuous line) with the change of the crystallinity (filled circles). The crystallinity data *vs.* temperature data of Ryan [9] was used to calculate the change in the crystallinity with temperature. The crystallinity data have been obtained by Ryan from the small angle X-ray scattering intensities recorded by syncrotron radiation.

The two experiments can theoretically not be directly compared. Firstly, because the HDPE sample used in the X-ray experiment is not characterised properly. Secondly, because the temperature of the material has been measured externally on the heating block and a 10 K min^{-1} heating rate was used during the records of SAXS and WAXS data. Therefore the temperature scale of the crystallinity experiment should be shifted to be able to compare the two sets of data. Nevertheless, the fit of the two independent data set is surprisingly good. The reversible heat flow (heat capacity) is shown in this Figure. The total heat flow, or the kinetic heat flow gave poor fits at the lower temperature part of the graph. The reversible heat flow has a sharper peak than the change in the crystallinity. The higher temperature parts follow more closely the kinetic heat flow (not represented on the Figure.).

Discussion

The reversing heat flow is always present during the melting process of semi-crystalline polymers. Its source is a relaxation type process [2]. Its portion within

the total melting enthalpy depends on the structure of the polymers. The greater the ratio of branched chains, the greater the reversible portion of the transition. Long time annealing (in the scale of min) irreversibly reduces the reversing heat flow but short time annealing (even by deep modulation with $p=15$ s modulation time) does not influence it markedly [1, 2].

There is a sharp decrease in the heat capacities during the annealing, particularly for PP, and this decrease is non reversible. It indicates some permanent changes in the polymeric system. If it is not the change in the crystalline part, it must be a change in the amorphous part.

There are hypotheses to explain what might happen during the annealing of semi-crystalline polymers [7, 10]. The hypotheses state, that there is a recrystallisation of polymeric chains from small crystalline particles to the bigger ones. This hypothesis is based on observation of lamellar single crystals [10] and it is seemingly supported by the small increase in the crystallinity after the annealing of bulk material. We have observed that the crystallisation does not take place during the annealing itself but in the following cooling process and we could not observe any growth in the degree of crystallinity so our observations do not support this hypothesis. (It is also questionable how can macromolecules diffuse from one site to the other one if they are not close to each others.) The unchanged (or even decreased) melting temperature of the annealed system does not support the diffusion theories of recrystallisation.

An exothermic heat flow is observed in the cooling section of a deep modulation carried out during the heating at the melting range of the polymers [1]. This indicates a true reversibility of the melting as there must be some crystallisation during the cooling. The crystallisation immediately follows the cooling, but there is no supercooling within the systems ($\Delta T<1$ K). Consequently, this crystallisation cannot be described by the known crystallisation theories [1] which all require supercooling of at least 10 K. Without supercooling the crystal should grow without essential material transport through a surface. This is possible,
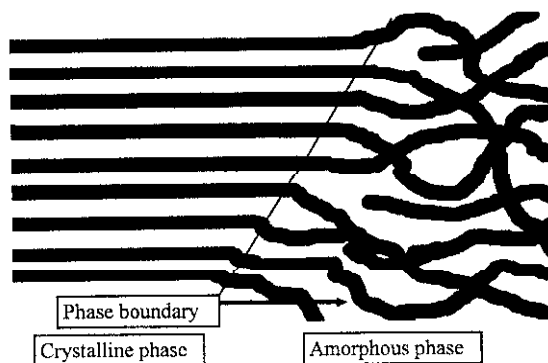

Phase boundary

Crystalline phase   Amorphous phase

Fig. 17 Strongly interacting (coupled) crystalline and amorphous phases of semi-crystalline polymers

when we allow crystal growth along the polymeric chain, i.e. from the portion of the tie molecules of the amorphous phase.

Figure 17 shows this way of crystal growth. The crystalline lamella is dominantly not a folded chain lamella it is much more likely to the fringed micelle. The phase boundary between the crystalline and the amorphous phases is at the lamellar surface. This is not a real surface as the amorphous phase is coupled to the crystalline one by chemical bonds at each polymeric chain. The plane of the phase boundary should not be perpendicular to the direction of the macro-molecular chains in the crystal due to the difference in the densities between the amorphous at the crystalline phase [6] (~15% according to the WLF conception [11]). Coupling means that the two phases are connected practically at each part of the phase boundary by chemical bonds therefore the thermal energy of one phase extends to the other one through vibrations. When the crystallinity changes, the surface is moving from the crystalline phase to the amorphous or v.v. without material transport between the phases.

The time necessary to achieve the final heat capacity values during the annealing is not more than several min. This is very fast change with respect to the changes in the crystalline phase suggested by Wunderlich [4]. As an exothermic event is observed on the cooling of the system an improvement of the crystallites during the annealing cannot be proposed. There is endothermic heat flow before the annealing. This means a decrease of crystallinity during the heating process (see also Fig. 16). This process is the formation of condis crystal according to the hypothesis of Wunderlich. The condis crystal with its conformational disorder would have greater heat capacities than the crystal itself. The rapid decrease of the heat capacities during the annealing indicates that the formed condis crystal disappears very quickly and the heat capacities reduce to the values that might be measured during the heating of the already crystallised system. This contradicts the concept of condis crystals, as the so-called new phase formed by the heating disappears in a short time.

The phenomenon can rather be explained like an interaction between a solvent and a solute. As there is no free surface along the phase boundary, the "melting" of the crystals (i.e. transforming molecular segments from the crystalline phase to the amorphous one) is much more a solution type process then a true melting. This process is a reversible one and it does not need supercooling to reverse it. The amorphous phase in a coupled state with the crystalline one shifts the phase boundary towards the crystalline portion upon heating. Then a conformational reorganisation within the amorphous phase can be processed during the relaxation period and the structure of the coupled chains fit more to the crystalline ones at the end of this process. This is a fast process with respect to the expected similar process in the crystalline phase.

Consequently, the reversible melting of polymers refers to the non-folded chain crystalline portion of the system.

Conclusions

The reversing heat flow during the melting process of semi-crystalline polymers is not a consequence of some kind of mesophase. It is due to the melting of crystalline particle in a strong interaction with their amorphous phase. The interaction is a kind of coupled thermodynamic system. The coupling is performed by the tie molecules transferring the amorphous phase from the crystalline phase. This is a solution like interaction where the amorphous phase is acting as a material which is different to the crystalline phase. In branched polymers this is a physical reality. The branched parts of the chain are chemically different from the parts within the crystals. In non-branched chains different conformation of the chains might result in a similar effect.

Annealing experiments lead to the conclusion that annealing modifies the amorphous phase rather then the crystalline one, making it suitable to arrange to the crystalline form at the cooling. This is again an indication that we have a coupled two-component thermodynamic system and the coupling is along the polymeric chain.

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