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Metastability in polymer systems studied under extreme conditions: high pressure, scan-iso T-t ramps and high scanning rates

Abstract

Laboratory measurements on polymer raw materials and products are often carried out (quasi-) isothermally, or at best at relatively slow cooling and heating rates. Such conditions differ greatly from those occurring during processing and during the product's use in real life. During processing, high cooling rates and high pressures are common, the parameters of which have a major influence on the most important forming processes, namely vitrification and crystallisation. In addition, polymer systems are highly metastable: all kinds of changes are possible as a function of time and temperature, such as reorganisation (via recrystallisation and annealing), cold crystallisation, solid-solid transitions, and superheating. Reorganisation phenomena can be hindered by applying high heating rates. Therefore, not only high cooling rates are required, but also techniques enabling high heating rates would be very welcome. In this review article, we will comment on the metastability of polymers under extreme conditions: high-pressure DSC and X-ray at hundreds of MPa's; scan-iso temperature (time ramps by DSC), and X-ray & high scanning rates as made possible by the recently developed High Performance DSC (HPer DSC). This is a generic name that encompasses quantitative measurement using controlled, linear scanning rates at hundreds of °C/min (high-rate DSC) in both the cooling and heating of (sub) milligram amounts of material. As such, it also facilitates high-throughput DSC.

Key words: *calorimetry, crystallisation, DSC, High Performance DSC, high rate DSC, high throughput DSC; high speed calorimetry, melting, heat capacity, enthalpy, crystallinity, real time, reorganisation, cold crystallisation, recrystallisation, X-ray*

1. Introduction

Before giving concrete examples of metastability in polymer systems and presenting some useful techniques and methods to study metastability, it is worth our while to specify the context in which these routes are being developed: the accumulation of know-how and expertise in the field of polymers via the 'chain of knowledge'. This means gaining insight via the natural route to the development of polymeric materials: starting from chemistry (polymerisation with a suitable catalyst and suitable reaction conditions) via processing to materials and products with certain desired physical properties, chemical resistance, durability and recyclability. Straightforward as this may seem, it is very difficult to optimise this chain. The development of a new, commercial polymer via this route takes 5 to 10 years easily, and production will often only be profitable after 10 to 15 years. In this regard, the situation in the polymer industry is similar to that in the pharmaceutical industry. This explains why there is a strong tendency to shorten the development route by blending existing materials and, in view of the recycling problems associated with blends, to use multi-purpose materials, such as all-polypropylene parts for the automotive industry. In the latter case, special product characteristics are obtained mainly through special processing methods. This mostly involves influencing the rheology and crystallisation during moulding in a targeted way, resulting in the desired morphology.

However, this calls for a thorough understanding of the 'chain of knowledge', and it will in fact be necessary to control the 'knowledge cycle'. By this, it is meant that not only is it important to relate polymerisation through processing to product properties with a minimum of trial and error, but that it is also crucial to master the reverse route, in other words to translate non-optimal properties into a more appropriate processing method, or even a more suitable macromolecular architecture. The advantage of controlling the 'knowledge cycle' – that is, of being able to reverse the normal development process – is a shorter lead-time in the development and optimisation of materials.

Figure 1 shows a cartoon of the 'knowledge cycle'. The symbols used are self-explanatory. The picture is of course greatly simplified, but the message is that the left half of the figure shows that the route from catalyst to properties works reasonably well, but that the reverse route (see the right half of the figure) – relating properties to processing conditions and, at a still deeper level, to molecular structure – barely exists. It is not difficult to sum up the missing information and possibilities. The points that need to be given attention in the near future have been formulated below as challenges in relation to the different roles associated with research groups at industrial companies and universities.

2. Different challenges for different groups

In general, for the coming decade, to our opinion the following challenges for academia, instrument companies and industry can be formulated:

Challenges for Academia: Know-Why
- Identify industry needs
- Develop basic knowledge and usable models
- Develop new characterisation techniques and methods

Challenges for Instrument Companies

- Develop dedicated instrumentation
- Develop new characterisation techniques and methods
- Develop user-friendly software and 'state-of-the-art' expert systems

Challenges for Industry: Know-How

- Challenge the academic community
- Have researchers who understand their university counterparts
- Bring the models developed 'down to earth'
- Translate ideas and findings into applications

3. Challenges for both academia and industry

Besides the issues listed above for the various target groups, there are a number of special challenges that will be of great importance for all those who work in the field of polymers in the coming decade. A number of these challenges are listed below. Some of the topics mentioned will be elaborated upon later.

Do Quantitative Research, Improve Modelling

- Use the two-phase model to the fullest, develop three-phase models

Aim at Conditions as Occurring in Practice

- such as those prevailing during processing
  - high pressure
  - high cooling rate
  - shear etc.
- Pay much more attention to dynamic cooling/heating conditions
- Handle complicated temperature-time ramps as in 'real life'

Perform In-Situ/Real-Time Measurements

- during processing
  - synchrotron X-ray
  - ultrasound, dielectric spectroscopy etc.
- matching processing
  - HPer DSC
- during polymerisation
  - AFM, spectroscopy etc.

Be Aware of Metastability and Low Order

- leading to reorganisation as a function of time and during heating
  - such as cold crystallisation
  - or recrystallisation
  - and annealing
- as a result of which, the connection between the morphology immediately after processing and subsequent measurements at higher temperatures is most probably lost.
  - Use solid-state NMR, real-time X-ray etc. (chart morphology)
  - Apply HPer DSC (chart reorganisation and restore connection).

4. Quantitative research and modeling

4.1. Use the two-phase model to the fullest, develop three-phase models

As an example of performing quantitative research using the two-phase model, the determination of some thermal properties is discussed, with the emphasis on the determination of quantitative, temperature-dependent crystallinities in cooling and heating within a reasonable time span, something best done by DSC. The two-phase model was developed for polymer research a long time ago and has been widely used [1]. From the point of view of Thermal Analysis & Calorimetry (TA&C), important quantities within the model are enthalpy-based mass crystallinity, baseline heat capacity and excess heat capacity. Baseline heat capacity represents the crystallinity-based contributions of $c_{pc}(T)$ (for the crystalline state) and $c_{pa}(T)$ (for the amorphous state) to the experimental $c_p(T)$. Excess heat capacity represents the contributions to $c_p(T)$ of changes in crystallinity. As both the polymer and TA&C [2,3] research branches have been very rapidly growing over recent decades, one might expect thermal-analysis software to be optimally geared to supporting polymer research, by inclusion of the important quantities mentioned. However, this is not the case. Until recently there was not a single commercial TA&C software package that incorporated the two-phase model and the associated crystallinity concept, which – as remarked – every polymer researcher uses as a first-order approximation. As a result, the two-phase model is not used to its full potential, and evaluations of TA&C measurements in this respect are just as qualitative as they used to be in the fifties. This lack of two-phase model software is remarkable, because back in the seventies pioneers like A. Gray (formerly Perkin-Elmer) and M. Richardson had already developed this kind of software. This is even more remarkable because, at the moment, TA&C is the only technique that can rapidly and quantitatively provide the temperature dependent crystallinities that polymer researchers need. Instrument manufacturers have no doubt reasoned that the demand for this kind of software was insufficient to justify its commercialisation. This point of view may be understandable, but it has effectively prevented TA&C from being used to its full potential in the development of polymeric materials. The two-phase model is undoubtedly the simplest model (see below). The company where one of the authors of this article is employed has been using more ad-

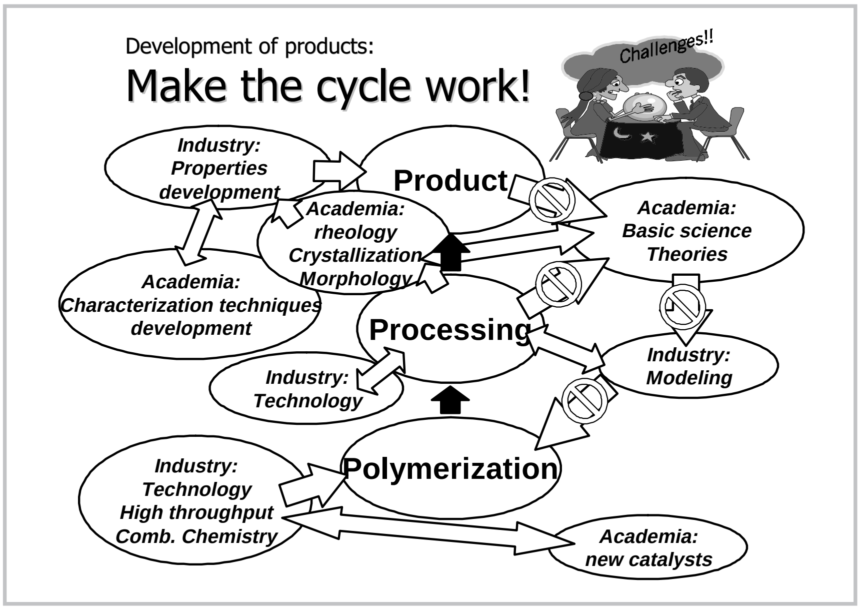

Figure 1. *Cartoon illustrating the roles of Academia and Industry and existing challenges with respect to the 'knowledge cycle' for the development of a polymer product from polymerisation via processing and optimisation via the reverse route. Links that do not work (well) are presented by* ⦸.

vanced models for over ten years; this was made possible by in-house software development. Recently a skeleton version of this software was commercialised [4]. It is suitable for any user, regardless of the type of instrument used. It should be noted that this is the first commercial software to use the ATHAS databank [5], which contains thermal data on many macromolecules. This databank should be a standard feature of all software supplied by instrument manufacturers. It is hoped that others will follow this example, and that cooperation between experts in the field and instrument manufacturers will bear fruit in the form of high-quality software. There is plenty of know-how available to raise the application of TA&C in polymeric materials and systems to a substantially higher level.

Figure 2 shows the results of 'pseudo-c_p' [1] DSC measurements on a series of homogeneous ethylene-propylene (EP) copolymers [6], as polymerised using a Vanadium catalyst [7,8], whose propylene content ranges from 4.4 to 35.3 mole%. The measurements show the extremely large influence of the propylene content on crystallisation and melting. Two effects can be observed: as the propylene content increases, the crystallisation and melting processes shift to lower temperatures, and the areas under the peaks become smaller. Obviously, propylene interferes with the crystallisation process in a major way, as is also obvious for ethylene-1-octene copolymers as produced with the same catalyst system [9].

Nucleation plays an important role in the crystallisation process during cooling for all samples [10,11]. The fast change in dq/dT at the onset of crystallisation in cooling for the less copolymerised samples (see Figure 2a) illustrates primary nucleation. When the temperature is decreased further, additional crystallisation takes place as a result of secondary nucleation and growth.

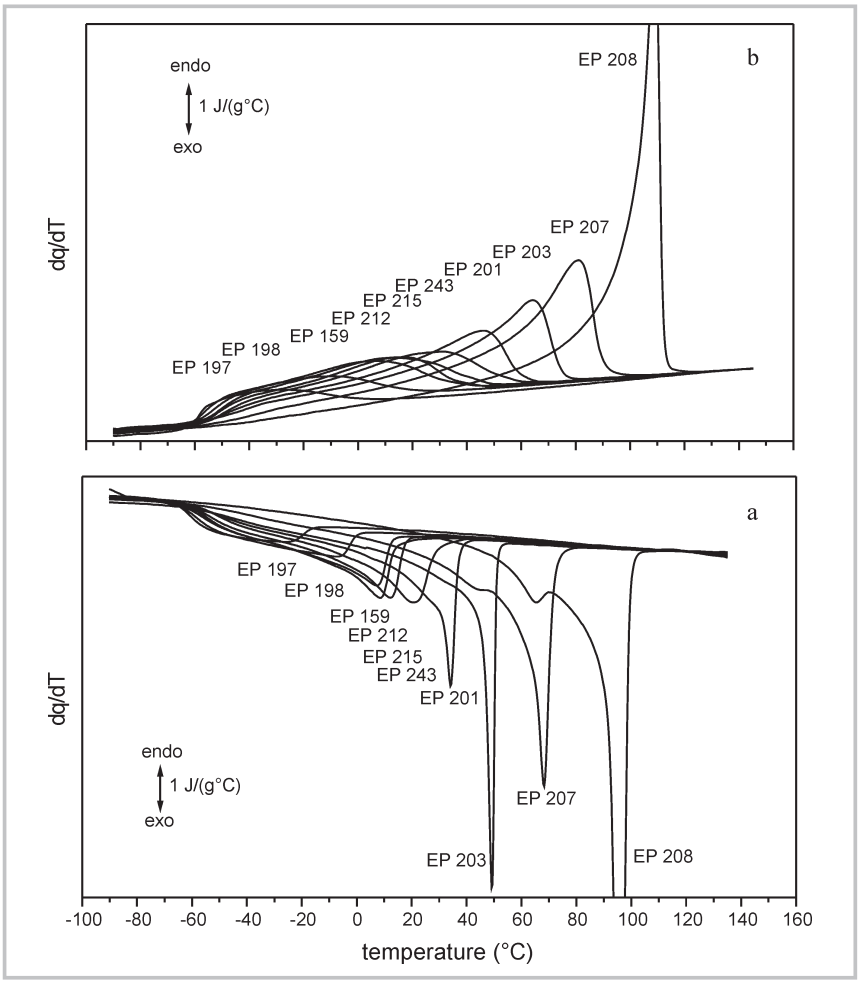

Figure 2. *DSC-2920 (TA Instruments) 'pseudo-c_p' cooling (a) and subsequent heating (b) curves at 10 °C/min in between –100 and 150 °C for homogeneous ethylene-propylene copolymers with varying propylene content (mole%): 4.4 (EP 208); 10.6 (EP 207); 17.4 (EP 203); 19.0 (EP 201); 22.2 (EP 215); 22.4 (EP 243); 24.7 (EP 212); 26.4 (EP 159); 30.8 (EP 198); 35.3 (EP 197). The curves were fixed at the same value at 120 °C (a) and 130 °C (b).*

In the case of the least copolymerised samples, such as EP 208 (4.4 mole% propylene) and EP 207 (10.6 mole% propylene), it is not immediately clear from the DSC curves when crystallisation stops. This is because for a (co)polymer, the heat capacities of the crystalline and amorphous phases are temperature-dependent, which means that even at constant crystallinity, dq/dT will never be constant, and this effect will need to be corrected for. As the co-monomer content increases, vitrification increasingly interferes with crystallisation. In the case of the more heavily copolymerised samples, for example EP 198 (30.8 mole% propylene), even an 'ordinary' DSC curve shows this, because for these samples the glass transition is clearly recognisable by the stepwise change in dq/dT at the lowest temperatures. For such samples, it is also visible that the melting process starts immediately after devitrification (see the DSC heating curves in Figure 2b). For the copolymers shown here, the glass transition temperature (taken as, for example, the point where the DSC curve shows an inflection, or determined using the enthalpy method [12]) decreases from about -35 to about -60 °C as the propylene content increases.

The observation of broadening DSC curves, lowering transition temperatures and decreasing DSC peak areas with increasing co-monomer content can be explained by the fact that a larger amount of short-chain branches, caused by the higher co-monomer content, reduces the capability to crystallise by shortening the length of the crystallisable ethylene sequences. As a result, crystallisation takes place at progressively lower temperatures, where chain mobility decreases as well. Hence, the chain segments are prevented from finding sequences of the same length, and so smaller, less perfect and less stable crystallites will form during crystallisation [13,14]. Both effects result in lower crystallinities with increasing co-monomer content, as confirmed by the decreasing peak areas.

The crystallinities as a function of temperature during heating, as calculated from the DSC heating curves of the EP (those given in Figure 2) copolymers and of some homogeneous metallocene-polymerised ethylene-1-butene (EB) copolymers, are shown in Figure 3 (a and b) respectively. During cooling from the melt, as soon as crystallisation starts, the crystallinity increases until it reaches a maximum value at the glass transition. In subsequent heating, crystallinity decreases during melting.

The cooling and heating curves in Figure 2 were measured using the 'continuous measuring method', which means that a single measuring run was carried out covering the entire temperature range of interest [1]. In the case of polymers this measuring method is to be preferred because – in the classical, 'stepwise measuring method' – every isothermal step can give rise to further crystallisation or melting as well as to reorganisation processes such as annealing, recrystallisation, etc. If such processes occur during an isothermal step, the measuring results are meaningless. Obviously, the 'continuous measuring method' imposes high demands on the stability of the calorimeter (prevention of drift) because there are only two calibration points (isotherms) left. The 'continuous measuring method' has yet another advantage in that it enables the use of high scan rates, for example to avoid recrystallisation, and in general to allow study of the kinetics of processes in a quantitative way [1,15].

The crystallinity curves included in the figures were determined according to the 'extrapolation method'. This method, which is extensively discussed and illustrated [1], and which can be universally applied with the aid of the software package [4] mentioned, uses extrapolation from the melt to estimate the contribution to the DSC signal of the (100%) amorphous phase. Such an extrapolation can be applied to c_p measurements; 'pseudo-c_p' measurements and even ordinary DSC measurements, provided there is no instrumental curvature, or no more curvature after correction. If this is combined with the temperature-dependent enthalpy reference differential function [1] (the enthalpy of transition) $\Delta h(T) = h_a(T) - h_c(T)$, which is known for many polymers (see the ATHAS databank) and in any case for polyethylene [1,16], the crystallinity can be calculated as a function of the temperature. The values found here are in good agreement with those obtained via the 'c_p method'. It is expected that the 'extrapolation method' will rapidly increase in popularity, for two reasons. In the first place, the demand for quantitative DSC measurements will increase because, as mentioned before, DSC is the only technique enabling rapid and quantitative determination of crystallinities as a function of the temperature. Moreover, other advanced techniques are also increasingly becoming available, for example real-time X-ray analysis with the aid of synchrotron facilities, so that results can be compared. Secondly, the above-mentioned software package makes the method suitable for any DSC user, regardless of the type of instrument used. So, obviously, for the copolymers discussed, the well-known two-phase model offers a useful first-order description of the morphology. However, for other polymers, several deviations from the two-phase model have been observed over the years. In particular, there is not always a one-to-one relationship between crystallinity and the jump in heat capacity in the glass transition region. The deviations observed are thought to be caused by molecules whose mobility is somehow hindered, even though they are entirely or partially located within the amorphous phase. For this reason, a three-phase model has been developed for describing the melting process, based on the assumption of additivity of enthalpies for fully crystalline, mobile and rigid amorphous phases [1]. It is assumed that rigid amorphous material behaves like vitrifying material during its formation. Like the two-phase model, this model too is capable of calculating the crystallinity, baseline heat capacity, and excess heat capacity as functions of temperature. It is of crucial importance that three-phase models, such as the one referred to here as well as more recent ones [17], will be developed and used by the polymer community.

5. Conditions as occurring in practice

5.1. High-pressure DSC measurements

As mentioned before, during processing a material may be cooled under high pressure. Particularly during injection moulding, pressures of a few hundred MPa's are quite normal. Measuring at such pressures is not easy, which explains why there are only a limited number of publications on DSC under high pressure, see e.g. [18, 19, 20, 21]. Figure 4 [22] shows that the peak melting temperature of a linear polyethylene (LPE) increases by approximately 100 ºC upon a pressure increase to 550 MPa, as is also the case for the peak crystallisation temperature (not shown). Homogeneous ethylene-1-octene copolymers with 2.1, 5.2 and 8.0 mole% octene show the same increase. But there is more. From literature [23, 24] we know that the crystallisation and melting of LPE is complicated, because during cooling at pressures above 200 MPa, the LPE molecules can crystallise from the melt in the hexagonal phase in extended form [25], leading to extended chain crystals (ECCs). Upon further cooling a transition from hexagonal to orthorhombic ECCs is likely to occur. At pressures lower than 200 Mpa, the

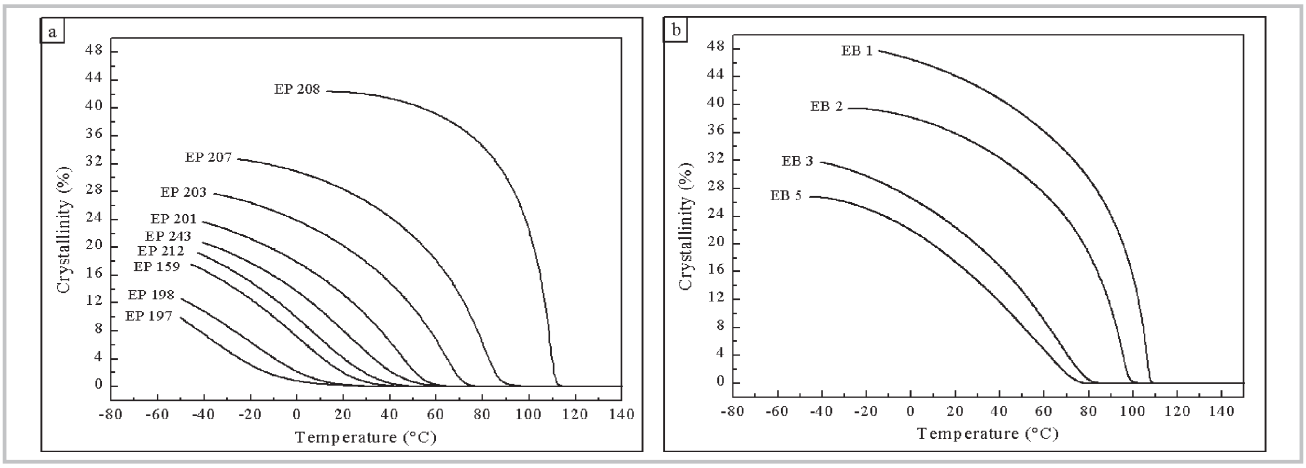

***Figure 3.** Crystallinity of homogeneous EP (a) and EB (b) copolymers as a function of temperature, calculated from DSC heating curves after cooling (all at 10°C/min) by extrapolation from the melt.*

chains fold during crystallisation in the orthorhombic phase, leading to folded chain crystals (FCCs). Extended chain crystallisation can take place because the molecules are sufficiently mobile at high temperatures, while the distances between the chains are also larger, so that they can be packed in alternative ways, for example in a hexagonal arrangement. On heating, any orthorhombic FCCs that are present melt first, which explains the small peak in Figure 4, indicated with the symbol I. At II, the large peak, we assume melting of orthorhombic ECCs and / or a solid transition from orthorhombic to hexagonal ECCs. At III the hexagonal ECCs melt. This peak is much smaller because the hexagonal phase is much more similar to the melt in terms of volume and enthalpy than the orthorhombic phase.

In the copolymers [26], peak III disappears with increasing octene content (see the copolymers with 5.2 and 8.0 mole%), probably because crystallisation and melting take place at increasingly lower temperatures, so that the mobility required for the hexagonal phase is increasingly lacking. This is in agreement with the fact that peak III moves towards peak II at reduced pressures, and ultimately disappears. Incidentally, at peak II we can no longer speak of ECCs, at most of EESCs, i.e. extended ethylene sequence crystals. The reason for this is that the co-monomer distribution gives rise to an ethylene sequence length distribution that constitutes the extreme limit of the possible crystal thicknesses. FCCs, peak I, now represent crystals with stem lengths that are (much) smaller than the ethylene sequence lengths. At the highest co-monomer content, 8.0 mole%, only peak I is still present.

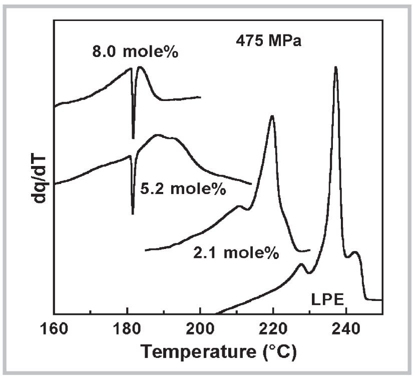

Figure 4. *Heating curves after cooling of the LPE and the copolymers having different 1-octene contents at 475 MPa; scan rate 10 °C/min.*

Surprisingly, in these copolymers totally new effects are observed that were not observed for LPE and HDPE. WAXD results, for example, point to the occurrence of disordering during pressurising to the same high pressures at room temperature [27, 28], an effect that resembles amorphisation [29, 30]. Upon cooling under pressure, the WAXD reflections appear to split. This is probably attributable to segregation according to sequence length and short chain branching into different crystal structures. In short, high pressure is a parameter that is important not only in industrial practice; it also gives rise to a large number of new effects that pose challenges to scientists and application developers. Here, too, it is important to complement DSC information with morphological studies, for example with the aid of X-ray analysis, performed under the same conditions, to obtain a detailed picture.

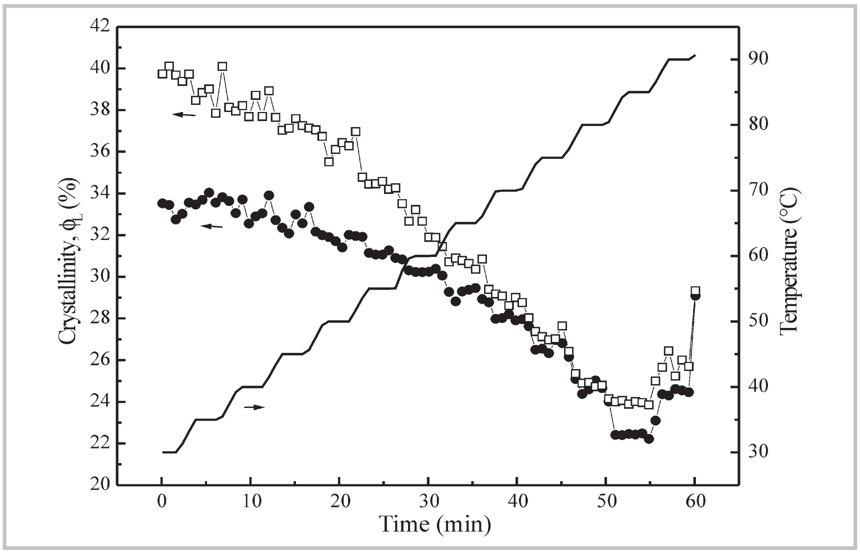

Figure 5. *The local volume crystallinity ϕ_L in the semi-crystalline regions, calculated on the basis of SAXS results, of the homogeneous metallocene-based ethylene-1-butene copolymer EB 2 cooled at 1 °C/min (☐) or quenched (●) from the melt during a (heating) scan-iso temperature-time program; (—) temperature.*

6. In-situ/real-time measurements

One of the greatest challenges for the near future will be in-situ and real-time measurement of processes. This holds true not only for processing, although currently the focus is on morphology development, for example during injection moulding. Techniques such as X-ray, ultra-sound and dielectric spectroscopy will hopefully create new possibilities in this field. However, during polymerisation also, it is very useful to study the interaction between polymerisation ⇔ crystallisation ⇔ morphology [31]: there are clearly gaps in our knowledge in this area. Techniques such as Scanning Probe Microscopy are likely to be of help in bridging these gaps [32]. This applies to the study of crystallisation and morphology in general: recently, lamellae growth during isotherm crystallisation was monitored for the first time [33]. For the time being, a great deal of progress can be made by combining different techniques and conducting the various measurements under the same conditions, particularly on samples with the same thermal history.

7. Metastability and low order

Polymers are generally highly metastable [34, 35]: the substances and materials studied are seldom in thermodynamic equilibrium. Hence, all kinds of changes are possible as a function of time and temperature: reorganisation [13, 36] by means of recrystallisation and annealing; cold crystallisation; solid-solid transitions; superheating, etc. [37, 38]. The same applies to pharmaceutical raw materials and products. This calls for research on the kinetics in the systems and on the metastability of these systems to be carried out. Such research will also yield a better insight into the behaviour of materials in real-life conditions.

7.1. Scan-iso temperature – time ramps by real-time (synchrotron) SAXS

Figure 5 gives an example of metastability, showing ‘scan-iso’ real-time (synchrotron) SAXS measurements [6] according to a temperature-time ramp that is comparable to a ramp that is also used in temperature-modulated DSC. Recently such measurements – which are essentially the same as the classical step-wise procedure for heat capacity measurements [1] – have also become known as ‘step-scan’ programs, and they can now be programmed via commercial software [39]. There are various interesting aspects to be observed. First of all the local (volume-fraction) crystallinity ϕ_L – which is the crystallinity in the semi-crystalline stacks of the homogeneous ethylene-1-butene copolymer – broadly decreases with increasing temperature, as is to be expected. It is striking, however, that in the quenched sample the crystallinity decreases less quickly than in the slowly cooled sample. The result is that, although the slowly cooled sample (naturally) starts with a higher crystallinity, the difference disappears at higher temperatures. This is confirmed by DSC and SAXS measurements [40, 41] on other copolymers, in which, over a certain small temperature range, the crystallinity of the quenched sample is even larger than that of the slowly cooled sample, and the same holds for the melting peak temperature. It was demonstrated that this is due to extensive recrystallisation of the quenched sample during heating, as a result of which this sample ‘caught up with the slowly cooled sample’ in terms of crystal thickness, crystallinity and melting temperature. Obviously, in such cases there is no point in trying to relate a crystal thickness at room temperature to a melting point via the Gibbs-Thomson equation [13, 38]. Apparently, there is a great deal of reorganisation going on in the sample – in this case via recrystallisation – during heating. This is by no means exceptional, so it is important not only to detect reorganisation, as in this case with the aid of X-ray analysis, but to prevent it where possible. This can be done by for example crosslinking the amorphous phase [2,42,43] and in particular by increasing the heating rate, see below: HPer DSC.

In the figure, the crystallinity follows the temperature-time program: it decreases during the heating scan and is constant during the isothermal stay. Characteristic quantities such as the amorphous layer thickness, and hence the long period, also follow the temperature-time program, and the same holds for the fraction of semi-crystalline regions. Obviously, in the absence of additional morphological information, such as WAXD and SAXS measurements under the same conditions [44, 45], it will be difficult to interpret results obtained by, for example, mechanical, spectroscopic and DSC measurements correctly.

7.2. Apply HPer DSC: chart reorganisation and restore connection

7.2.1. High Rate DSC: a tool to study metastability

We shall now report on measurements performed with a so-called **High Performance DSC (HPer DSC)**, which was recently developed [46, 47] specifically for the study of metastable systems. To this end, the dynamic range of standard DSC was considerably extended to include rates of a few hundreds degrees per minute. This aspect of HPer DSC can be referred to as High Rate DSC, a particular form of high-speed heating calorimetry [15,48,49,50,51,52,53,54,55,56], where even much higher rates are realised. In heating, hundreds of degrees per minute does not seem spectacular, for any power compensating DSC or heat flux DSC can achieve such rates. However, in contrast with existing equipment, the HPer DSC enables us to achieve *controlled and linear scan rates in heating as well in cooling.* At the high rates, calibrants such as indium, lead, zinc, adamantane, azoxyanisole etc., retain the peak shapes as recorded at low rates, provided that the sample mass has been adjusted to (sub-)milligram level. Furthermore, hardware and software adaptations are required.

Figure 6 illustrates an advantage of the use of a high heating rate, in this case 100 °C/min (HPer DSC), compared with 10 °C/min (standard DSC). After cooling of a polyethylene terephthalate (PET) at 10 °C/min, during which the sample partially crystallises and subsequently vitrifies below approximately 85 °C, it is clearly observable that in heating at 10 °C/min cold crystallisation occurs to a considerable degree, followed by melting of the sample. Of course, we know how to interpret such a situation [1], and also how to correct the enthalpy of fusion for the contribution relating to cold crystallisation. This is not difficult, certainly if the above-mentioned software package [4] is used. However, things can be simplified much further, see the heating curve measured at 100 °C/min. Evidently, this rate is high enough simply to *prevent* cold crystallisation. As a result, the endotherm that is measured gives a straightforward representation of the melting of crystals formed during cooling. So, there is no longer any interference with cold crystallisation processes resulting from the macromolecular chains’ ability to crystallise during heating. Of course, it is still meaningful to measure at different heating rates if one wishes to chart the kinetics and metastability of the sample. After all, here too it is very interesting to compare the two heating curves. It is clear, however, that a high heating rate adds considerable value.

7.2.2. High Performance DSC: heat capacity measurement at high rate

The answer to the question as to which combinations of scan rates provide useful information depends on the research objective and on the specific sample. If, in the case of the PET sample, the aim is to relate the DSC results to, for example, the material’s behaviour under injection moulding conditions, higher cooling rates [56, 57, 58, 59, 60] should of course be applied. At a cooling rate of 100 ºC/min, the sample in question already appears not to crystallise all the way down to the glass transition. This need not always be the case: addition of nucleating agents, etc. can induce crystallisation even at this cooling rate. The sample mass is typical: 1.285 mg. Comparison with the reference values for amorphous and completely crystalline PET according to the ATHAS data bank (see dotted curves) shows that the cooling curve at 10 ºC/min is not quantitative, while the heating curve is quite good. This is typical of measurements of this kind with standard DSC equipment: cooling imposes greater demands on the equip-

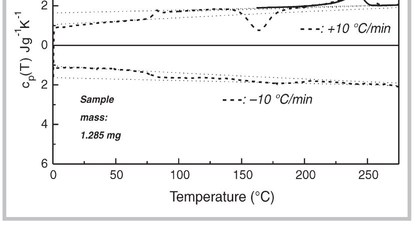

Figure 6. *High Performance DSC (HPer DSC), using a modified PerkinElmer Pyris-1 calorimeter, on a polyethylene terephthalate sample. Crystallisation and vitrification during cooling at 10 °C/min; devitrification, cold crystallisation and melting during subsequent heating at 10 °C/min. Heating at 100 °C/min suppresses cold crystallisation: only melting is seen.*

ment. In this case, the low sample mass is the cause of the problem: for a heat capacity measurement in cooling at 10 ºC / min a higher sample mass must be used, and / or the DSC must be stabilised further. However, this experiment was not aimed at performing a heat capacity measurement in cooling at 10 ºC / min; the c_p axis refers to the measurement at 100 ºC / min. The fact that the heat capacity is measured offers opportunities for a further, quantitative analysis of the curve measured at 100 ºC / min. Integration of this curve yields the enthalpy curve, and by comparing the results with the reference values we can calculate the crystallinity as a function of the temperature.

So, an important aspect of HPer DSC has to be emphasised: the decrease in dQ / dt resulting from a low sample mass – which is necessary to avoid extra thermal lag arising – is compensated for by the high scan rate. Moreover, since the measuring time has been shortened drastically (in this case to less than 3 minutes), instrumental drift is effectively suppressed, so that quantitative measurements are possible. Thus, the technique offers the unique possibility to perform heat capacity measurements at rates of more than a hundred degrees per minute, both in cooling and in heating. In this way, an important aim is achieved: HPer DSC does indeed offer high performance at high rates.

7.2.3. High Throughput DSC: a tool for fast characterisation of minute amounts of material

An extreme example of a low sample mass measurement is given in Figure 7, which shows how quantitative information could be obtained from a 29 µg HDPE sample at scan rates of 150 ºC / min. Not only could the crystallisation and melting point distributions be measured [61], but also the heats involved could be established, which is new and unique. The sample was obtained via fractionation using SEC; the polymer in the elute was solidified on a rotating germanium disc using a Lab Connections (LC) transform module [62]. Thus, seven fractions, ranging in sample mass from 8 to 100 µg, could be measured in a quantitative way by FT-IR and HPer DSC. With the aid of FT-IR, the average branching content along the molar mass distribution was measured, while an analysis of the crystallisation / melting behaviour with the aid of HPer DSC provided complementary information about the distribution of the branches influencing that behaviour. The fraction (No. 7) shown is the lowest molar mass fraction (200 to 2000 g / mol) of the HDPE. The method opens up tremendous possibilities for studying the crystallisation / melting behaviour of fractions, as obtained by any available small-scale fractionation method. Recently, a UHMWPE sample of just a few µg was measured, and no problems with signal to noise, curvature etc., were encountered. Of course, careful handling is required in weighing and manipulating such tiny samples.

In general, the low sample mass needed – at milligram level down to micrograms – in combination with a high sensitivity and resolution opens up quite different applications. To mention some of the systems which are now brought within reach: coatings and very thin layers, for example in multilayer films; heterogeneities in samples, such as gels, additives, etc.; and tiny amounts of sample produced by fractionation techniques as shown. Thus, fast screening by High Throughput DSC of minute amounts of material as produced in combinatorial chemistry has been shown to be possible.

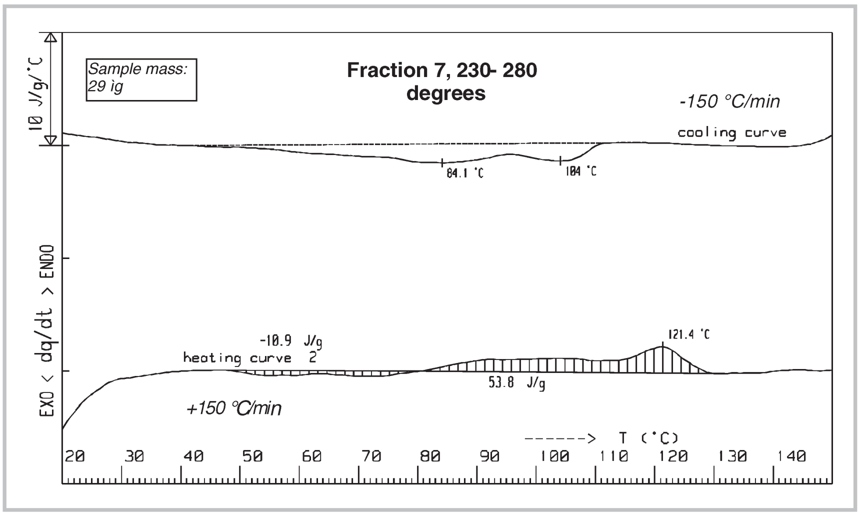

Figure 7. HPer DSC cooling and subsequent heating curves at 150 °C/min for a 29 µg HDPE sample, obtained by fractionation of a butene-containing High Density Polyethylene (HDPE), of 0.45 mg in total, by Size Exclusion Chromatography (SEC).

8. Conclusions

These examples show that interesting new developments are taking place with respect to scanning calorimetry. First of all, it is clear that modern equipment permits the carrying out of quantitative measurements, provided the equipment is sufficiently stabilised, the conditions are well chosen, the available models and data banks are used, and the results are properly evaluated.

Real-time morphological studies – in particular with the aid of scanning probe microscopy (AFM and its variations), small-angle light scattering (SALS) and synchrotron X-ray (WAXD and SAXS) – carried out under conditions similar to those usually applied in DSC (incl. TMDSC), provides the required insight into the phenomena measured with DSC.

A development that will be of great practical benefit and scientific interest is high-pressure (here, up to 550 MPa) DSC. It will be of practical benefit because several important processing techniques (such as injection moulding and extrusion) involve high pressures (up to a few hundred MPa’s). It is of scientific interest because pressure is an important and hitherto scarcely investigated parameter. It is challenging from an industrial point of view because it may be expected to open up new polymer applications.

DSC has a unique potential for studying the metastability and associated kinetics of polymeric and pharmaceutical systems, owing to the large dynamic range that can be achieved, from (quasi) isothermal to dynamic measurements at hundreds of degrees per minute with the aid of High Performance DSC (HPer DSC).

HPer DSC, a new form of calorimetry, offers the possibility of applying controlled (linear) scan rates up to several hundred degrees per minute in both heating and cooling and will undoubtedly become a very important tool.

It will play a crucial role in relating laboratory results to processing conditions, because it offers the possibility of measuring at high cooling rates. It will also be crucial in suppressing reorganisation (cold crystallisation; recrystallisation, annealing etc.) during heating by means of high heating rates. In general, it will be of great value in the study of the temperature-time dependence of important processes such as vitrification and devitrification, crystallisation and melting, solid-solid transitions, etc. It can do all this and still offer a high performance: since the measuring time is reduced to minutes, instrumental drift is negligible. Therefore, even heat capacity measurements are possible at the high rates. As the required sample mass can be extremely low – from milligrams to a few micrograms – it is also possible to analyse impurities, coatings and the yields of analytical fractionations and combinatorial chemistry experiments: HPer DSC can also be used as High Rate DSC and High Throughput DSC.

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