

# Thermal analysis and calorimetry beyond 2000: challenges and new routes<sup>☆</sup>

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## Abstract

A brief overview is given of developments in thermal analysis and calorimetry (TA&C) in the last few decades. The overview is followed by a discussion of the trends anticipated, the (un)desirability of these trends and the actions that need to be taken. Over the last few decades, the popularity of TA&C has increased at an impressive rate. However, educational institutes are paying less and less attention to analytical expertise, including TA&C. This means the number of *practitioners* is steadily decreasing and TA&C is increasingly becoming a ‘purely analytical tool’ for *users*. Moreover, TA&C is seen as a simple and cheap method which has reached the limits of its potential. It seems that the success of TA&C is having a paralyzing effect, causing developments to stagnate. Due to the lack of practitioners, there is not enough technology push to drive new developments that are of a scientific rather than commercial interest, and there threatens to be a lack of contact between the TA&C community and the scientific community. As a result, the competence level of TA&C users threatens to decrease, simply because there are fewer examples of ‘state of the art’ TA&C work in the form of studies and publications, and because the number of training facilities is decreasing. This is an alarming trend. Suggestions are offered for reversing this trend and a proposal is made for a concrete approach to ensure that the necessary actions with regard to TA&C will be implemented via National Societies for Information, Communication and Education and National Expertise Centers for Development. The quantitative capabilities of TA&C and past and future developments are illustrated with reference to polymers on the basis of examples of quantitative DSC, high-rate calorimetry, high-pressure DSC, real-time X-ray and SALLS and temperature-modulated reaction calorimetry. The combining of TA&C and scanning probe microscopy (SPM), with the aim of providing time- and position-resolved analyses of materials, is discussed as an example of a promising development.

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## 1. Characterization of eras

The following is a personal view on developments with regard to thermal analysis & calorimetry (TA&C). Obviously, this view is to a large extent determined by the context in which it was developed. My point of departure was the situation in the BeN-

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eLux countries (Belgium, the Netherlands and Luxembourg), which is more or less representative of a large part of Europe. It would be highly illuminating to investigate the situation in other parts of the world and communicate this in the present journal or via the International Confederation for Thermal Analysis and Calorimetry in the ICTAC News. However, I am convinced that the views expressed below have a wider significance because the developments and trends outlined — both technical and scientific — transcend national boundaries and the world is increasingly becoming one big marketplace. I hope to provide at least a development scenario for those countries where the situation is not yet so serious and where the downward trend may be reversed if we succeed in charting a new course in time.

I will start by giving an overview of developments in TA&C in recent years.

### 1.1. The 1970s

The 1970s showed a shift from TA&C equipment built in-house to commercial TA&C instruments. In addition, a start was made on the computerization of TA&C. TA&C groups become dependent on producers: only a few groups continued to do development work under their own steam.

### 1.2. The 1980s

In the 1980s the number of suppliers of DTA equipment decreased. The range of commercial equipment was expanded to include microcalorimetry, reaction calorimetry and coupled equipment (GC-FTIR-MS, TGA-DSC-MS, DSC-microscopy). The use of sample exchangers increased. Software packages were adapted to suit new (highly diverse) computers but did not always offer new possibilities. The number of TA&C users continued to increase, even in research groups whose main line of research was not in TA&C. TA&C was greatly popularized.

### 1.3. The 1990s

The 1990s saw the emergence of low-cost equipment. One of the few new developments in this period was temperature-modulated DSC, which has become very popular. In addition, simultaneous measurements

as made possible by real-time WAXS-SAXS-DSC, using synchrotron facilities, have opened up new perspectives for research on materials. TA&C is coming within the reach of smaller companies, which use it for quality control, troubleshooting and competitor analysis. In large companies, TA&C is used in local as well as central research organizations for supportive research relating to quality control, troubleshooting and competitor analysis and for innovative research into processes, base materials, materials and products.

A development which had already started in the 1980s clearly manifested itself in the 1990s, namely, a sharply declining interest in the development of methods and techniques and, more generally, a declining interest in analytical disciplines at universities and research institutes. One of the reasons for this is that companies and governments are increasingly pushing (and financing) these institutes to carry out research on materials. When resources are scarce, choices have to be made, and in such cases, analytical research is usually the victim. As a result, it is increasingly up to the instrument suppliers rather than research groups to initiate new developments. In Europe in particular, the decline in the interest in new analytical techniques is accelerated by the generally waning interest in the exact sciences, in particular chemistry and physics. Admittedly, analytical research sometimes has a rather dusty image and therefore does not appeal much to students.

The remaining university research groups that are (still) contributing substantially to the development of analytical methods and techniques fall into two categories:

- groups that continue to exist because they are led by scientists — ‘*practitioners*’ — who have built up an excellent reputation and whose contributions to science and to their institute are generally acknowledged to be outstanding. However, the continuity of many of these groups is in danger because their leaders are approaching retirement age and successors are unlikely to be appointed. This problem is becoming acute in the BeNeLux countries and in Western Europe in general;
- groups whose work is of (supra)national importance by virtue of their specialization in a particular, very expensive technique. Examples are synchrotron facilities and high-field NMR. Some-

times national interests play a role in maintaining such groups, for example, when a country considers it desirable to enhance its knowledge infrastructure by forming or maintaining research groups that can provide advanced support in special areas. The groups usually have access to considerable financial resources.

What is the situation with regard to TA&C? Everyone knows that it is a centuries-old discipline and that the equipment is relatively cheap and easy to operate. Moreover, the output seems to be readily interpretable. So, why should highly qualified researchers spend any effort on further developing it? To some extent, this reasoning is understandable. After all, the popularity of TA&C has greatly increased since the 1980s, as is illustrated by the situation in the Netherlands. The Dutch national TA&C organization, TAWN, saw its membership double to about 300 in only 10 years. Every year about 10% of these members are transferred to different jobs, which means that every year there are about 30 new ‘users’. TA&C courses organized by instrument suppliers and training institutes attract many participants. So why worry about the future of TA&C?

It is not that the people who carry out TA&C work (often alongside their other analytical activities), whom we here refer to as ‘users’, are doing a poor job. On the contrary, the quality of their work is highly acceptable, considering the knowledge and know-how available to them. Moreover, they are supplied with equipment and training by manufacturers who pay a lot of attention to quality. The reason, then, why should we worry about the future of TA&C concerns two other aspects:

- will the ‘users’ be able to obtain support from experienced top experts, ‘practitioners’, when they face complex problems or need follow-up training or special equipment?
- is it desirable that progress in TA&C will depend *exclusively* on the efforts of instrument suppliers?

By this last point, I emphatically do not wish to imply that these suppliers are doing a poor job. Everyone will agree that their role is important and should be continued.

But it is a cause for concern that as the number of practitioners and their research groups decreases, the

remaining developers — the instrument companies — will focus on maximizing the sales of their products, which is only natural. This means that developments that are not of commercial interest will be discontinued, even though they may be highly relevant from a TA&C point of view. This is bound to reduce the number of options available to users, not only as regards hardware (instruments) but also as regards software.

The trend sketched above is one of the reasons why the development of software has stagnated for several years. This is not to say that software developers have not kept pace with developments in the software industry (Windows, etc.) and improved aspects such as user-friendliness and reporting and presentation facilities; major advances have been made in these fields. In 1974, when the author of this article joined an industrial company, he found a research environment which was greatly underdeveloped as far as computerization and automation were concerned: computer-controlled on-line measurements, which were becoming quite common at universities, were still unheard-of in industry. The PC was yet to be invented, of course. But industry gradually made up for the ground it had lost, and nowadays many industrial laboratories feature robust stand-alone measuring units, often with multi-tasking configurations, which are increasingly integrated into local computer networks.

The problem is that the software improvements of the last few years are only superficial and have not kept pace with the theoretical advances made. The following Intermezzo (see Appendix A) will illustrate this.

#### *1.4. Intermezzo I: heat capacity, enthalpy, crystallinity, baseline and excess heat capacity*

The fact that TA&C hardware and software are not sufficiently developed is also apparent from the lack of diversity in the products offered. This is because most applications are too small-scale to be commercially interesting. As a result, totally different user groups are treated alike and supplied with hardware and software which is (too) general-purpose in character. This is an extremely regrettable development. It represents a denial of the fact that the needs of an operator who is in charge of at-line control of product speci-

Table 1  
Summary of developments

Outline of developments up to 2000	
1950–1980	1980–2000
Producers: technology push	Producers: technology push
Practitioners: technology push/market pull	<b>A missing link</b>
Users: market pull	Users: market pull
Producers: education of instrument users	Producers: education of instrument users
Practitioners and societies: ad hoc education	Societies: ad hoc education
Individualized $\Rightarrow$ general-purpose hardware. Software development	(Too) <b>general-purpose hardware and software</b>

fications differ from those of a researcher who is evaluating a new material. Unfortunately, this rather obvious observation has not led manufacturers to differentiate between target groups.

This leads us to an important conclusion, namely that new developments in hardware, software and training courses should be geared much more to different target groups.

If the trends described above are not reversed, they will inevitably lead to a situation in which TA&C will develop from a specialization of practitioners into a ‘purely analytical tool’ for users (Table 1).

## 2. The near future

### 2.1. The years 2000<sup>+</sup>: what can we expect?

- If the current trends persist, we may expect a further increase in productivity, for example, as a result of an increase in the use of sample exchangers in DSC and TGA apparatus.
- Small production companies will have at-line quality control and troubleshooting facilities based on DSC and TGA using sample exchangers. The software should support measurements carried out in accordance with standard procedures such as DIN and ASTM. Companies will increasingly be under pressure to seek certification to, for example, ISO standards.
- In small development companies we may expect applied research & technical development (AR&TD) and research & development (R&D) to be supported by DSC; TGA(-MS); DMA (/TMA) using sample exchangers.
- Large companies will have facilities like the ones mentioned for the small production companies for

their production sites; they will have business support groups for AR&TD using facilities like those used by small development companies. Their central or corporate research departments will use techniques such as DSC; temperature-modulated DSC; high-T DTA; photo DSC; DSC thermomicroscopy; (high-resolution) TGA(-MS); GC-FTIR-MS; cone calorimetry; microcalorimetry; reaction calorimetry; TMA; DMA; DETA; heat conduction/diffusion measurement capabilities.

- A large company’s central research department will typically use expensive, complicated, varied equipment and equipment that is shared between several business units. Their research activities will require a high level of scientific and technical expertise. In addition, large companies will feel a need for an intermediary for specific measurements by outside institutes:  $pVT$ ; heat conduction; high pressure; extreme cooling and heating rates; time-resolved WAXS-SAXS-DSC using synchrotron radiation. The *raison d’être* and viability of a top-level TA&C group in an industrial company will to a large extent depend on whether that company has a central research facility, and this in turn will largely depend on the desired synergy between the company’s business units.

### 2.2. The years 2000<sup>+</sup>: what needs to be done?

Many people think that TA&C has reached the limits of its potential and that hardly any new developments are to be expected — apart from a few exceptions such as TMDSC. This is a wrong view which, however, threatens to become a self-fulfilling prophecy if no action is taken.

Therefore, I should like to give my personal (modest) list of challenges which our discipline should try to meet (most examples are related to DSC, but similar challenges can and *should* be worked out for other techniques).

First of all, the development of methods and techniques is essential. This is the responsibility of both producers and expertise centers, see below. In this connection, the following aspects are important.

### 2.2.1. Use present capabilities to the full

For both scientific and industrial uses, dynamic measurements (meaning measurements at specific scan rates) are required because the aim is to imitate production processes, to assess the degree to which processes are kinetically determined and, for practical reasons, to limit the measuring time as much as possible. The assessment of the kinetic determinacy of processes is particularly important in the case of polymeric systems, because in these systems the metastability of morphological entities plays a major role, leading to reorganization, annealing, recrystallization, superheating, etc., see Intermezzo II (Appendix B). These phenomena can, moreover, also occur in plastic products during use. They are also important for the interpretation of DSC curves obtained, because during heating as well as during cooling all sorts of changes can occur which make it difficult to interpret the measuring results. This strongly depends on the sample history (especially the thermal history), the scan rate chosen, etc. One way of avoiding reorganization effects is to increase the scan rate, while the amount of reorganization can be established by varying the scan rate. In this way the quality of the interpretation of the results can be improved. A major advantage of DSC compared with other techniques is that DSC measurements can be carried out under *dynamic conditions*. In this regard, too, TMC offers interesting possibilities because it enables the range of possible scan rates to be extended to lower (average) values. Other techniques are (fortunately) catching up by allowing measurements to be carried out under dynamic (scanning) conditions. It is already possible to carry out real-time small angle laser light scattering (SALLS) measurements, and also real-time X-ray measurements with the aid of synchrotron facilities, in which scan rates of 10°C/min are readily feasible, see Intermezzos II and III (Appendices B and C).

Performing  $c_p$  measurements under dynamic conditions [1] across wide temperature ranges should be the standard procedure. Analysts should strive — where possible — to determine excess and baseline heat capacities. Quantitative measurement of heat changes should become routine too: at present DSCs are quite often being used as expensive thermometers. This is a direct consequence of the fact that TA&C is sometimes practiced at a low level and that calorimeters are not always stable enough because of temperature drift, etc.

### 2.2.2. Intermezzo II: metastability and kinetics: reorganization, recrystallization and recovery

#### 2.2.3. Improve existing equipment

Increase the throughput per DSC: several measuring cells per DSC equipped with sample exchangers combined with the flexibility of time–temperature ramps. Develop cheaper and more robust measuring cells (aggressive chemicals, longer life). Improve DSC stability considerably to enable unattended operation with sample exchangers by reducing temperature drift, by carrying out an empty pan correction for imbalance, etc. More attention should be paid to cooling under controlled conditions; in most equipment much emphasis is placed on heating while the importance of measurements during cooling is given less attention or even neglected. In particular for applications in materials science, better heating and cooling possibilities with adjustable and guaranteed scan rates are very important for the study of (de)vitrification, crystallization and melting.

The improvement of other existing techniques, such as X-ray, SALLS, solid-state NMR, etc., towards real-time measurements, see Intermezzo III (Appendix C), would be very useful for providing the proper background for the interpretation of (dynamic) thermal analysis measurements, especially DSC measurements, as DSC is an inherently ‘fast’ technique, see Intermezzo II (Appendix B).

#### 2.2.4. Intermezzo III: real-time morphology measurements

#### 2.2.5. Develop new equipment

Temperature-modulated DSC (TMDSC) has several advantages compared with conventional DSC. It

offers the possibility of determining the frequency dependence of thermal properties, for example, and it is more sensitive at very low ‘underlying’ scan rates or under ‘quasi-isothermal’ conditions. Moreover, it offers an alternative way of determining heat capacities and it makes it possible to distinguish vitrification from processes like cold-crystallization, curing, etc. For TA&C users it is important to be able to choose between various instruments, preferably from different producers. The emergence of TMDSC [2–5] is an excellent example of a successful publicity campaign for a technology-push invention. A lot of work still has to be done to perform correct measurements and to interpret the results correctly. This is because the way in which the measurement is carried out (a response in temperature to a variation in temperature, with the risk of properties being influenced), and therefore also the interpretation, is intrinsically more complex than in the case of DMA and DETA. For future developments it is important that the frequency range be increased. Hopefully, multi-frequency calorimetry [2] will also become a possibility. For some applications, for example, the separation of vitrification and chemical reactions or cold crystallization, temperature modulated calorimetry (TMC) offers important new possibilities, and it will no doubt also be used in combination with microcalorimetry and reaction calorimetry, see Intermezzo VI (Appendix F). In other cases, such as the performance of heat-capacity measurements and the interpretation of melting, it is doubtful whether TMC will live up to the expectations, with the exception of the quasi-isothermal mode of measurements. Analysts who are at present unable to perform quantitative  $c_p$  measurements should not expect to be able to perform them with the aid of TMC because the quality of the results will still depend on the analyst’s skills, the calibration of the calorimeter, the shape of the sample, etc. In general, the intrinsically low ‘underlying’ scan rates and quasi-isothermal measuring methods of TMC are mainly of importance for fundamental studies.

As is illustrated in Intermezzo II (see Appendix B), in some cases extremely high heating rates are required to avoid reorganization phenomena. An interesting development in this direction is found in the scanning adiabatic (thin foil) calorimeter. One should be aware that some production processes involve extremely high cooling rates. For these rea-

sons, instruments allowing cooling and heating rates of up to 10,000°C/min and higher would be very welcome and would tremendously increase the potential of TA&C.

#### 2.2.6. *Intermezzo IV: thermal diffusivity and conductivity*

It is regrettable that it is virtually impossible to carry out TA&C measurements at high pressures, for example, from 100 to 10,000 bar. Such measurements would be highly relevant, because pressure is an important parameter, not only from a theoretical point of view but also in industrial practice, where processes conducted under atmospheric pressure are the exception rather than the rule. It is a pity that there are only a few DSC instruments in the world that can be operated at high pressures. Of course, in order to be able to work at high pressures major experimental problems have to be solved. This is typically a field that should be explored by an ‘expertise center’ because the market demand for high-pressure instruments will be limited, which means that instrument manufacturers will make no effort to meet this demand. Such development work should be done through international cooperation. And once they have been developed, the availability of high-pressure facilities should not be limited to one or two countries, see Intermezzo V (Appendix E).

#### 2.2.7. *Intermezzo V: high-pressure DSC*

One of the fields in which we may expect considerable growth is process and safety research. Companies are increasingly making efforts to reduce the environmental impact of their operations (via energy and process optimization) and generally show increased safety awareness (prevention of runaway reactions). To support their efforts in these fields they need special measuring facilities, ranging from a very small scale (micrograms and milligrams) as achievable with DSC, through gram scale (microcalorimeters) and kilogram scale (reaction calorimeters) to full-scale tests. The instruments should be flexible with respect to reaction conditions (pressure, agitation, mixing; measuring of fast reaction and type of reactants, etc.) and it should be possible to monitor processes with the aid of various techniques (IR, etc.). In this field, too, Temperature-Modulated Reaction Calorimetry has a lot of potential, see Intermezzo VI (Appendix F).

### 2.2.8. *Intermezzo VI: Temperature Modulated Reaction Calorimetry*

At-line and in-line measurements are becoming increasingly important for controlling production processes. The possibilities offered by thermal-analysis techniques in this field are usually confined to at-line analysis. However, there are opportunities on the horizon for in-line analysis, for example, by combining of DETA with processing equipment. A very important application of at-line and in-line measurements is high-throughput screening as applied in combinatorial chemistry. The possibilities offered in this field will have a major impact on development routes in the life sciences and material sciences.

Last but not the least: miniaturization on a micrometer/nanometer scale is expected to expand the possibilities for analytical support in a major way. This concerns not only in-line processes but especially the combination of time- and position-resolved analysis of materials. By this I mean the analysis of materials on a (sub-)micrometer level. Heterogeneities on a (sub-)micrometer scale are often crucial to the behavior and properties of polymer systems, and the possibility of probing a material on such a scale will be of great interest. It would be logical to combine such analyses with scanning probe microscopy (SPM). Several combinations are currently being developed, such as SPM-pyrolysis-GC-MS; SPM-spectroscopy, SPM-solid NMR and SPM-deformation behavior. The first qualitative results obtained with SPM-thermal analysis at micrometer level have already been reported [6,7]. A recent development<sup>1</sup> is the 3D-image reconstruction of the morphology of layers with a thickness of 10  $\mu\text{m}$ , via scanning probe microscopy using a thermal tip. The sample is scanned at a number of modulation frequencies: high frequencies provide information corresponding to the superficial layers, lower frequencies additionally include deeper structures. The reconstruction is based on the sensitivity matrix approach adapted from electrical impedance tomography, a medical imaging technique. The possibility of carrying out research on such a scale or even on nanometer scale via real-time measurement

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<sup>1</sup>A European Community sponsored (Esprit) program: high-power computing (HPCN)-enabled tomographic analysis with scanning microscopy (TASM).

of temperature and heat changes would open up great perspectives. We can only speculate about the ultimate scope and impact of developments in this field.

### 2.2.9. *Turn black boxes into gray/white boxes for hardware and software*

In order to enable TA&C analysts to select the right equipment for research, producers should provide more hard data than they have done until now. For quality reasons as well as for product-liability reasons, a lot more information should become available about the functioning of the instrument, and manufacturers should supply specifications that are much more detailed and give better proof of the reliability of the measurements. Uniformity in specifications as regards accuracy, sensitivity, etc. is necessary and organizations like ICTAC should strive to achieve this. In addition to ‘smoothed’ data, raw data should also be available, as well as information about manipulation of data. How long do we have to wait until all manufacturers provide means for measuring the temperatures of the sample (or rather the sample sensor), the reference and the oven? Any instrument supplier aspiring to a high-quality status should provide such data of its own volition. And if a firm is hesitant to provide these data this should be a major reason not to buy that firm’s instruments.

### 2.2.10. *Improve measuring, manipulation and presentation of data*

Multi-point temperature and heat calibrations should be made possible. It should also be possible to correct for differences in scan rates without making the results any less insightful. Statistical process control methods should be introduced. Multiple time-temperature ramps should be made possible. Multi-tasking possibilities should be provided as regards measuring and evaluating. It should be possible to link various brands of TA&C equipment in a local network, with an option to link up to bigger networks. Databases, e.g., the ATHAS database, should be incorporated into the software as a standard feature. Standard settings in accordance with DIN, ASTM, etc. should be included. With a view to structuring and securing data storage, archiving systems should be compatible with the software currently available and mass-storage facilities should remain readable

for at least 10 years (which is still much less than the 20 years which would be preferable for patent reasons). Measured data should be compatible with commonly used evaluation software. Reporting facilities (for processing and storing text and measuring results) should also be compatible with the available software.

#### 2.2.11. Software packages incorporating state-of-the-art models

Enthalpy and crystallinity determinations should become standard options in DSC, see Intermezzo I (Appendix A). Having measured these quantities, the thermal analyst's next goal is quantitative determination of the excess and baseline  $c_p$ . Two- and three-phase models should be incorporated into the software. Determination of enthalpy-based glass transition temperatures, see Intermezzo II (Appendix B), should be included in all software. And so on, see Intermezzo VII (Appendix G).

#### 2.2.12. Intermezzo VII: three-phase models needed

### 2.3. Back to the near future: conclusions

TA&C has become so common that its success is now having a paralyzing effect: development is stagnating. There are scarcely any groups with TA&C as their main activity. As a result, there is too little top-level TA&C work. There is yet another reason why development is stagnating. Users are unable to work in a scientifically sound way as commercial instruments have hardware and software restrictions and are black boxes and because users can rely less and less on support from experienced groups of practitioners. This is aggravated by the fact that few training courses in TA&C are offered on a structural basis, while the number of practitioners that might provide training is decreasing. Apart from this there is a trend towards a situation in which students get to know TA&C only during their practicals, if at all, while the link between TA&C and thermodynamics will remain obscure to them. These future executives — the decision-makers — will consider TA&C to be a purely analytical tool. The general opinion will be that TA&C has no potential for further development any more, resulting in a money/brain drain to new techniques. This doom scenario will lead to a downward spiral.

I should like to stress once again that the trend described above is one which affects all analytical disciplines and should therefore be a reason for the research communities at universities and in industry to thoroughly review their policies. These communities should become aware that they threaten to lose one of the preconditions for progress in their chosen fields of research, namely good analytical support. We are facing the threat of a general shortage (at least in Europe) of qualified researchers in chemistry and physics. In addition, analytical researchers as a group have a low status. As a result, the number of analytically oriented university graduates is disconcertingly low, and things will only get worse because several chemistry and physics research groups will soon cease to exist. Many companies are already forced to train their researchers 'on the job' in analytical fields of expertise. The only way out of this downward spiral is that universities again accept their educational responsibilities in this field. But this will happen only if industrial companies explicitly ask them to.

### 2.4. Towards a better future: 2000–2005

So what are the keys to changing the present undesirable situation? It is realistic to expect that universities and companies will (continue to) see TA&C as a 'tool' and that without targeted actions the development of TA&C will stagnate. We can nevertheless work towards a better future in various ways.

We should aim to ensure the optimum use of TA&C in research and production by raising the level of users via education and by stepping up the development of methods and techniques [9].

- First of all we should try to achieve improvements in the field of *education*, in the broadest sense of the word. I already mentioned the useful role of instrument suppliers with regard to training in the use of their products, but what is lacking in many countries is permanent and well-structured training facilities which offer students the opportunity to either broaden or deepen their knowledge in the field of TA&C. The fact that several relevant subjects have disappeared from the university curricula, for example, thermodynamics [10], does not make it easier for TA&C professionals to



improve their skills other than via training ‘on the job’. As indicated above, one would expect universities to accept their responsibility in this regard, but as far as this is concerned little change is to be expected in the foreseeable future. Therefore, for the short term it would be wise to focus on a pragmatic approach and investigate what educational role *national TA&C societies* might play. An important thing to bear in mind is that *training courses should be geared to the needs of different target groups*.

- Secondly, the *development of techniques and methods* is of crucial importance for the future of TA&C. Not as a goal in itself, but based on the insight that TA&C could have an even bigger impact on socially and industrially relevant research than it has at present. An important precondition for this is a ‘*technology push*’ from *practitioners*, whose approach to new developments and opportunities in their field of expertise is not purely commercial. But for the instrument suppliers, too, it is important to be able to consult top researchers and research teams on cutting-edge developments with regard to techniques and methods. In the present constellation it is realistic to assume that these top researchers and top research teams will disappear if no targeted action is taken. In some countries these groups can be counted on the fingers of one hand, and within a few years from now many groups will have disappeared. This is no exaggeration. One of the few remaining options open to us is to reinforce or build *expertise centers*, preferably at universities. At these centers, *know-how in the field of TA&C should be concentrated and made available to users*. These

users will provide the necessary market pull. It is probably realistic to expect there will be room for only very few of such centers per country.

If users can rely on support from practitioners in expertise centers, this can have several advantages. For example, analysts in small firms and in industrial laboratories are expected to master several techniques, which means they will seldom acquire the in-depth knowledge which is required in some applications. When they are faced with such applications, it is desirable for them to be able to consult a central expertise group (within or outside the company). And a production lab, an application lab or a troubleshooting lab is usually equipped with only the most essential instruments. Such labs should be able to have special measurements carried out elsewhere. It is of course perfectly normal for an expertise center to charge a fee for such services. Moreover, the frequency with which an expertise center is asked to perform such services or make available its infrastructure is an excellent performance indicator. And finally, it would only be logical if expertise centers played a role in education and training, see Intermezzo VIII (Appendix H).

#### 2.4.1. Intermezzo VIII

A development along the lines sketched above might lead to the situation depicted in the Table 2:

#### 2.4.2. Gear actions to target groups

As mentioned earlier, it is necessary to differentiate between the various target groups, each of which has its own hardware and software needs. The various groups also have widely different training needs. For

Table 2  
Summary of developments

Outline of developments up to 2005

1950–1980	1980–2000	2000–2005
Producers: technology push Practitioners: technology push/market pull Users: market pull Producers: education of instrument users Practitioners and societies: ad hoc education	Producers: technology push <b>A missing link</b> Users: market pull Producers: education of instrument users Societies: ad hoc education	Producers: technology push <b>Expertise centers: technology push</b> Users: market pull Producers: education of instrument users <b>TA&amp;C societies: structured education for target groups</b> <b>Hardware and software split up for target groups</b>
Individualized ⇒ general-purpose hardware. Software development	(Too) general-purpose hardware and software	

example, newcomers need hands-on start-up training and tips and tricks from practitioners, while experts need to be able to delve deeply into the subject matter, understand the links with thermodynamics and exchange opinions and ideas with fellow professionals. The first type of training course should be given close to the user, whereas the second one demands international coordination. Between the novices and the experts there is a very large target group consisting of professionals with several years' experience.

### 3. A concrete approach

Based on the foregoing, I propose the following actions:

1. More attention should be devoted to *education*: bring TA&C users up to standard and maintain them at standard. Also, stimulate market pull by users via education. National societies should regard education as one of their main tasks. What is needed is a structured approach geared to specific target groups, rather than ad hoc initiatives;
2. Initiation of *technology push* by practitioners, also in cooperation with producers. Setting up of expertise centers at national levels to promote technology push, the aim being top-level research and development based on expert know-how and skills in the field of TA&C.

These actions aimed at securing the necessary developments in TA&C might be implemented via

1. National societies for information, communication and education.

As mentioned earlier, the TA&C user profile has changed considerably. Therefore, we should first of all ask ourselves the following questions:

- Do the national societies (still) know their members?
  - Has this been structurally researched? Compare the survey by Wunderlich [10].
  - Are the members' needs known, including those in the educational field?
2. National expertise centers for development.  
What would be the ideal situation? An expertise center

- with which the national society forms an alliance;
- to which universities and industries can have recourse;
- where users can be (re)trained.

I firmly believe that, in the long term, the answer to the question (see Footnote 1) 'Thermal Analysis & Calorimetry: is familiarity breeding contempt?' will be negative only if National Societies change their course and take the actions needed as soon as possible.

### Acknowledgements

The author would like to thank his colleagues at DSM Research (M. Pijpers, R. Scherrenberg, J. Smeets, E. van der Vegte) and at the Katholieke Universiteit Leuven in Belgium (S. Vanden Eynde, B. Goderis, H. Reynaers) for their stimulating cooperation over the years.

### Appendix A. Intermezzo I

#### A.1. Heat capacity, enthalpy, crystallinity, baseline and excess heat capacity

Take, for example, the models used in research on polymeric materials. These models were developed a long time ago and are widely used nowadays. Polymer research is a very rapidly growing branch of research and one might expect thermal-analysis software to be optimally geared to supporting this research. However, nothing could be farther from the truth. Until recently there was not a single commercial software package that incorporated the two-phase model and the associated crystallinity concept which 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 are often just as qualitative as they used to be in the fifties. Important quantities within the model are the enthalpy-based mass crystallinity, the baseline heat capacity and the excess heat capacity. The baseline heat capacity represents the crystallinity-based contributions of  $c_{p_c}(T)$  (for the crystalline state) and  $c_{p_a}(T)$  (for the amorphous state) to the experimental  $c_p(T)$ . The excess heat capacity represents the con-

tributions to  $c_p(T)$  of changes in crystallinity. The lack of two-phase model software is remarkable, because back in the 1970s pioneers like A. Gray (who was then working for Perkin–Elmer) and M. Richardson had already developed this kind of software. And it is even more remarkable if we bear in mind that 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 commercialization. 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. And the two-phase model is only the simplest model! The company where the author of this article is employed has been using more advanced models for over 10 years; this was made possible by in-house software development. Recently a skeleton version of this software was commercialized [11].<sup>2</sup> It is suitable for any user, regardless of the type of instrument used. Moreover, in line with the objectives of the ICTAC Education Committee, efforts have been made to make this software available worldwide at minimal costs. It should be noted that this is the first commercial software to use the ATHAS databank (for a recent description see [12] and for ATHAS databank 1980: see [8,64]). 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.

We shall first discuss the possibilities offered by true  $c_p$  measurements with reference to the ethylene–propylene copolymer EP 207 [13], see Fig. 1. The cooling and heating curves in Fig. 1a were measured using the ‘continuous measuring method’, which means that a single measuring run was carried out

which covered the entire temperature range of interest [14]. 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 crystallization or melting as well as to reorganization processes, such as annealing, recrystallization, 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. In Fig. 1b cooling and heating curves for EP 207 obtained via the ‘continuous measuring method’ are compared with those obtained according to the classical ‘stepwise method’. Differences can be observed on the high-temperature side, from about 40°C upwards. The step size was 25°C, except between 60 and 100°C, where a step of 35°C was required to obtain an acceptable signal or to be able to introduce an isothermal stay. On the low-temperature side the results are in good agreement, especially if we take into account that the measurements were carried out on two different DSC-7 instruments. Clearly, stepwise measurements are not suitable for polyethylenes if there is a substantial  $dq/dT$ , but we are interested only in processes in which there is such a  $dq/dT$ . The ‘continuous measuring method’ has yet another advantage in that it enables the use of high scan rates, for example, to avoid recrystallization and in general to be able to study the kinetics of processes in a quantitative way [15].

Fig. 1a successively shows crystallization and vitrification in cooling (downward curve) and subsequent devitrification and melting in heating (upward curve). In both cases, (positive)  $c_p$  values are obtained. Now how do we decide where crystallization stops during the cooling run and where melting begins during the heating run? Likewise, one may wonder whether the heats of crystallization and melting and the crystallinity can be determined and if so, how. In the case of polymers these questions can be answered [14] and the procedure is in fact straightforward, provided the two-phase model is applicable. Even when three phases are present (e.g., when an additional rigid amorphous phase is present [14,16], there are possibilities for determining the heats of crystallization and melting and the crystallinity, but in that case a suitable (mor-

<sup>2</sup>The ‘Temperature Dependent Crystallinity software program’ which runs under Windows 95/NT has been developed by DSM Research BV and Anatech BV jointly, which program is available through Perkin–Elmer.

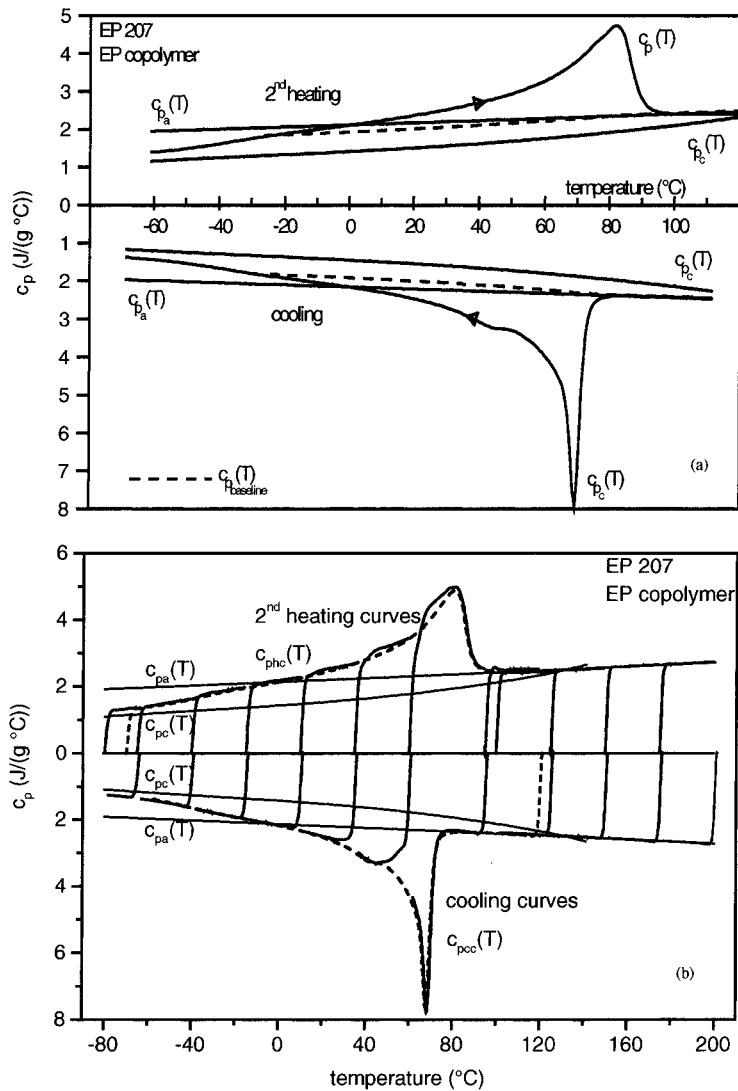


Fig. 1. DSC-7 specific heat capacity curves,  $c_p(T)$ , at 10°C/min for EP 207 obtained in cooling (downwards) and subsequent heating (upwards); the reference curves for the amorphous phase,  $c_{p_a}(T)$ , and for the crystalline phase,  $c_{p_c}(T)$ ; and the baseline curves,  $c_{p_b}(T)$  (---) (a) continuous specific heat capacity curves between -70 and 120°C; (b) continuous and step-wise specific heat capacity curves between -70 and 120°C and between -80 and 200°C, respectively.

phological) model needs to be postulated. For the ethylene copolymers under review here, the two-phase model has been found to be adequate. This model is based on the assumption that the sample can be divided into 100% crystalline and 100% amorphous regions; for a detailed discussion see [14]. Another assumption is that the enthalpies of these regions are additive according to mass fraction. For a large

number of polymers the heat capacity reference functions for the 100% crystalline and 100% amorphous regions,  $c_{p_c}(T)$  and  $c_{p_a}(T)$ , respectively, are known [8,12,64].

Fig. 1 shows not only the experimental heat capacity curves but also the  $c_p$  reference curves for polyethylenes [13,17,18]. In the melt part of both the cooling curve and the heating curve,  $c_p(T)$  and

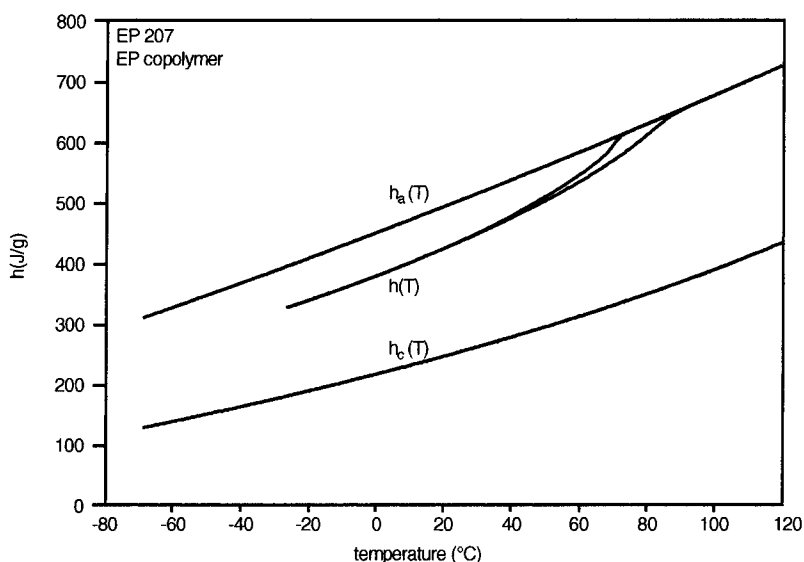


Fig. 2. Specific enthalpy cooling curve, subsequent heating curve and reference curves  $h_a(T)$  and  $h_c(T)$  for EP 207, based on the specific heat capacity curves shown in Fig. 1a.

$c_{pa}(T)$  coincide, which illustrates that  $c_{pa}(T)$  provides meaningful information. The figure also shows that in this region the experimental curves are symmetrical with respect to the temperature axis. These similarities are important and sensitive quality criteria for  $c_p$  measurements.

Fig. 2 shows the enthalpy reference functions,  $h_a(T)$  and  $h_c(T)$ , respectively [17,18]. These enthalpy curves can be calculated from  $c_{pc}(T)$  and  $c_{pa}(T)$ , respectively, by simple integration, together with the heat of melting at the equilibrium melting temperature,  $\Delta h(T_m^0)$ . In this figure, the cooling and heating curves coincide at low temperatures (in other words, they form a closed cycle), which is an indicator of the quality of the measurement. It is important to realize that all reference curves are temperature-dependent, and hence also the heat of melting  $\Delta h(T) = h_a(T) - h_c(T)$ , which is sometimes called the enthalpy reference differential function. Depending on the polymer, the value of the heat of melting at room temperature or at the glass transition temperature may be as low as 50% of the heat of melting at the equilibrium melting temperature.

We shall now discuss the calculation of the crystallinity as a function of the temperature [14]. Assuming, as mentioned above, that the two-phase model is valid for EP 207, we may assume additivity of the enthalpy

contributions for the two phases — amorphous and crystalline [14]:

$$h(T) = w^c(T)h_c(T) + w^a(T)h_a(T) \quad (\text{A.1})$$

where

$$w^c(T) + w^a(T) = 1 \quad (\text{A.2})$$

With the aid of these two expressions we can define the (temperature dependent) enthalpy-based mass fraction crystallinity,  $w^c(T)$ , below  $T_m^0$ , the equilibrium crystal-melt transition temperature:

$$w^c(T) = \frac{h_a(T) - h(T)}{h_a(T) - h_c(T)} \quad (\text{A.3})$$

For EP 207 the maximum crystallinity at  $-20^\circ\text{C}$  is about 32%, see Fig. 3. Fig. 3 also includes the mass crystallinities calculated from real-time WAXD measurements [13]. For this particular copolymer the results obtained with the two techniques are still in good agreement and any discrepancies are probably due to thermal lag problems with the synchrotron measuring set-up. In this figure, as in Fig. 2, the DSC crystallinity curves form a closed cycle. The curve once again shows that the crystallinity at room temperature is a rather arbitrary point, which is meaningful only in the case of applications at room temperature or if a comparison is made with a mea-

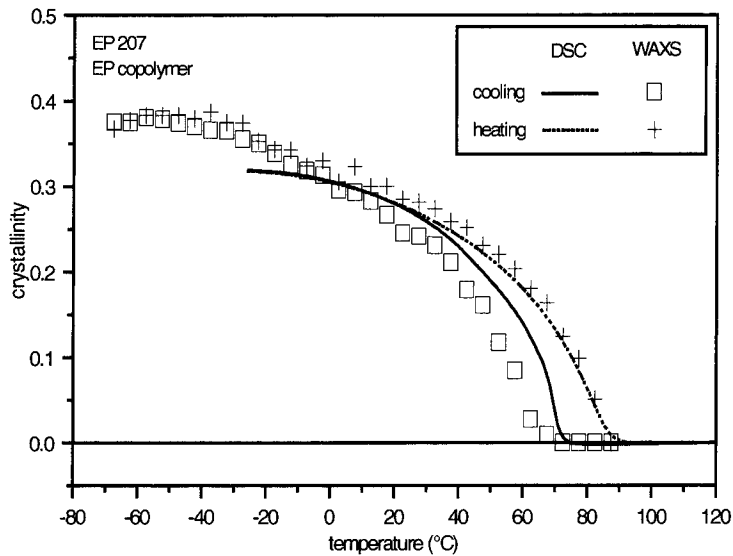


Fig. 3. Enthalpy-based mass crystallinity curves based on DSC (as calculated from curves shown in Fig. 3), and mass crystallinity curves from WAXD, for cooling and subsequent heating at 10°C/min for EP 207.

surement carried out at room temperature, for example, a crystallinity value based on density, an X-ray measurement, etc. However, the only way to obtain real insight is to carry out a measurement as a function of temperature, and it is in such cases that DSC has proved to be one of the few techniques available for quick and quantitative determination of temperature-dependent crystallinities. It should be noted that for the samples we have studied we have always found a good agreement (typically better than 3% absolute) between mass crystallinities calculated from  $c_p$  and density measurements.

Especially in crystallinity calculations, the temperature dependence of enthalpies should be taken into account. So it is incorrect to assume a fixed value, for example, the value at  $T_m^0$  which is often used, because the crystallinities thus obtained may well be too low. In the case of polyethylenes, the deviation may well be more than 10%, and with other polymers deviations of up to 30% are possible. In such cases a comparison with the crystallinities obtained using other methods is meaningless and the data cannot be used as a basis for determining whether or not an interphase or third phase is present.

It is also clear that the measurements shown in Fig. 1 alone are not sufficient for determining the heats of crystallization and melting. For such determinations

the so-called excess heat capacity curves need to be determined. This can be done by subtracting the so-called baseline heat capacity curves from the curves measured. The procedure has been described and applied earlier [14,19]; we shall only give a brief overview here.

Differentiation of  $h(T)$  in Eq. (A.1) with respect to temperature

$$c_p(T) = \left( \frac{dh}{dT} \right)_p \quad (\text{A.4})$$

yields

$$c_p(T) = w^c(T)c_{p_c}(T) + h_c(T) \frac{dw^c(T)}{dT} + w^a(T)c_{p_a}(T) + h_a(T) \frac{dw^a(T)}{dT} \quad (\text{A.5})$$

$$c_p(T) = w^c(T)c_{p_c}(T) + [1 - w^c(T)]c_{p_a}(T) - [h_a(T) - h_c(T)] \frac{dw^c(T)}{dT} \quad (\text{A.6})$$

The  $w(T)$  terms are regarded as belonging to the 'baseline' heat capacity and the  $dw(T)/dT$  terms as belonging to the 'excess' heat capacity:

$$c_{p_b}(T) = w^c(T)c_{p_c}(T) + [1 - w^c(T)]c_{p_a}(T) \quad (\text{A.7})$$

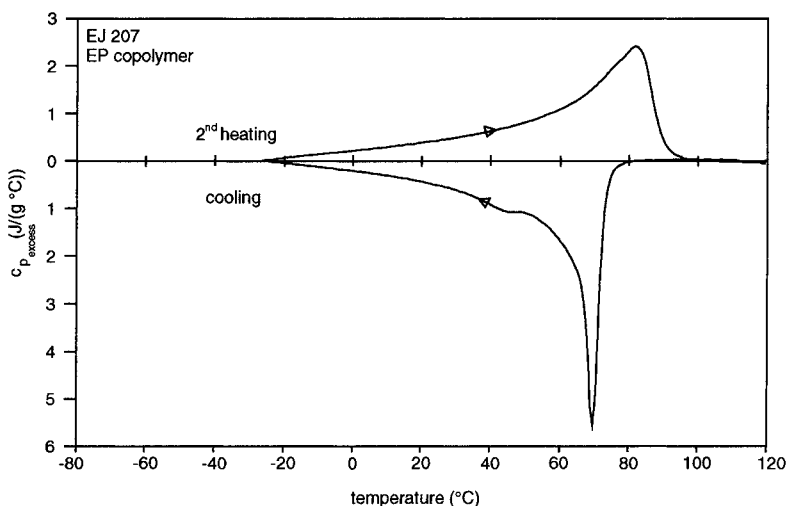


Fig. 4. Specific excess heat capacity curves for EP 207 for cooling and subsequent heating at  $10^{\circ}\text{C}/\text{min}$ , as calculated from measurements shown in the preceding figures.

$$c_{p_e}(T) = -[h_a(T) - h_c(T)] \frac{dw^c(T)}{dT} \quad (\text{A.8})$$

and

$$c_p(T) = c_{p_b}(T) + c_{p_e}(T) \quad (\text{A.9})$$

The baseline heat capacity reflects the contributions of the temperature-dependent  $c_{p_a}$  and  $c_{p_c}$  to the experimental  $c_p(T)$  via the crystallinity. In Fig. 1a the resulting baseline heat capacity curves are plotted for EP 207. These differ not only from each other but (of course) also from the reference curves. The points where they intersect with the measured curves indicate the temperatures where, in a cooling run, crystallization ends (because vitrification interferes with the crystallization process) and, in a heating run, melting begins (because the mobility of the chain segments increases due to devitrification).

The excess heat capacity reflects contributions such as (re)crystallization, annealing and melting — processes by which the crystallinity is changed — to the experimental heat capacity. The first part of the right-hand member of Eq. (A.8), the enthalpy reference differential function  $h_a(T) - h_c(T) = \Delta h(T)$ , is known for many polymers, see for example, the ATHAS databank [8,12,64]. The second part, the change in crystallinity with temperature  $dw^c(T)/dT$ , can be numerically calculated from  $w^c(T)$ , which function is given by Eq. (A.3).

Fig. 4 shows the excess heat capacity curves for EP 207. It is clear that crystallization and melting take place above about  $-25^{\circ}\text{C}$ . By determining (partial) areas under the cooling and heating curves at a specific temperature we can obtain *the* heats of crystallization and melting, respectively, at that temperature for EP 207 at the given history. Of course, this determination method is equivalent to the determination in Fig. 1a of the (partial) areas enclosed by the baseline curves and the measured curves. The excess curves are actually the most interesting ones because these are by definition related to changes in crystallinity. Therefore, theoretical models should be able to predict or describe these curves.

We will now illustrate the use of the ‘extrapolation method’ for calculating crystallinities as applied to ‘pseudo heat capacity’ measurements. In ‘pseudo- $c_p$ ’ measurements [14], which are an alternative to heat capacity measurements, one and the same empty-pan measurement is subtracted from all pan+sample measurements in order to obtain a first-order correction for instrumental curvature of the DSC curves. This is necessary because measurements with instrumental curvature are useless for determining a heat of transition or crystallinity. In pseudo- $c_p$  measurements no absolute  $c_p$  scale is aimed at. If the energy calibration is not (very) temperature-dependent, for some calorimeters it suffices to carry out a single sapphire

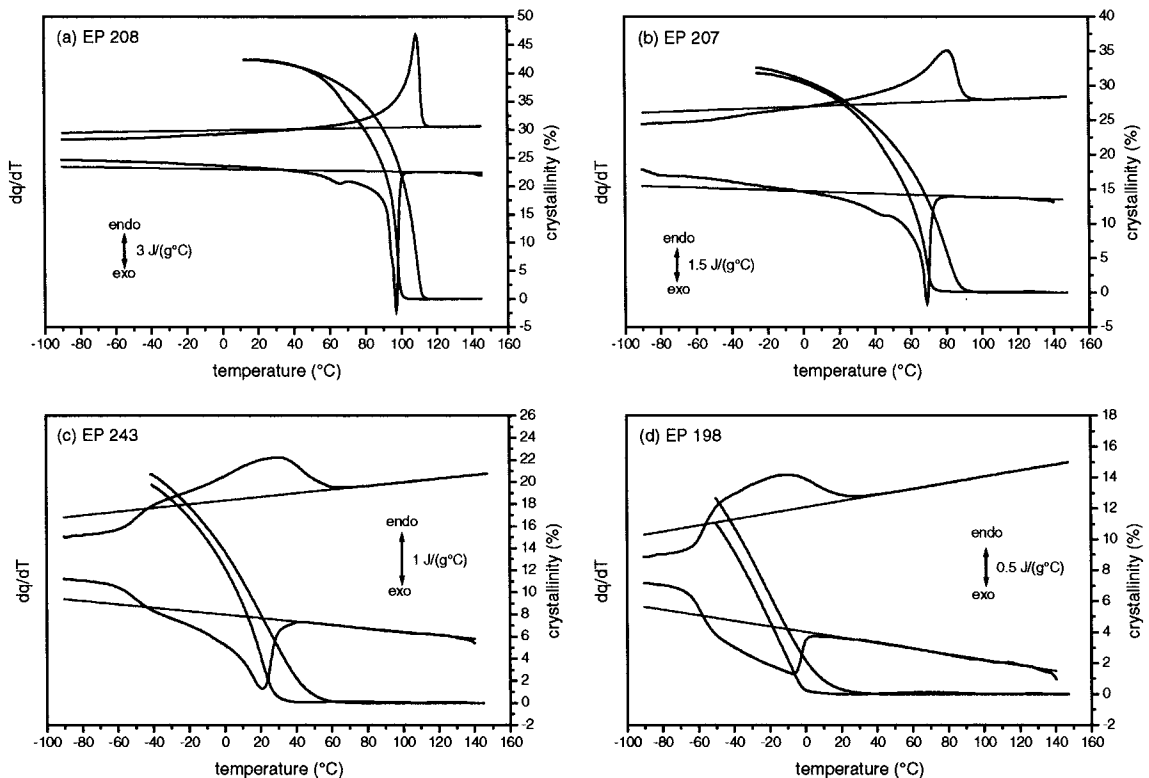


Fig. 5. DSC-2920 pseudo- $c_p$  cooling (downwards) and subsequent heating (upwards) curves at  $10^\circ\text{C}/\text{min}$  in between  $-100$  and  $150^\circ\text{C}$  for homogeneous ethylene-propylene copolymers with varying propylene contents (mole%). (a) EP 208 (4.4%); (b) EP 207 (10.6%); (c) EP 243 (22.4%); (d) EP 198 (30.8%). The curves are located vertically arbitrarily. Also shown are the crystallinity curves for cooling and subsequent heating, as based on the pseudo- $c_p$  measurements, according to the ‘extrapolation method’.

calibration or even an indium calibration. This means the measurements are easier to carry out than a true  $c_p$  measurement. It has been found in practice that such measurements nevertheless yield acceptable results that provide satisfactory answers to most questions.

In Fig. 5a–d, a number of characteristic samples are shown [20] on which measurements were carried out according to the above-mentioned ‘pseudo- $c_p$ ’ method. Some samples have been extensively discussed above (EP 207, 10.6 mole% propylene) and elsewhere (EP 243, 22.4 mole% propylene, in [21]; EP 198, 30.8 mole% propylene, in [13]) on the basis of  $c_p$  measurements. The crystallinity curves included in the figures were determined according to the ‘extrapolation method’. This method, which is extensively discussed and illustrated in [14] and can be universally applied with the aid of a recently developed software package [11] (see Footnote 2), 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 not any more. If we combine this with the temperature dependent enthalpy reference differential function  $\Delta h(T) = h_a(T) - h_c(T)$ , which, as stated earlier, is known for many polymers and in any case for polyethylene, we can calculate the crystallinity as a function of the temperature. The values found here are in good agreement with those obtained via the ‘ $c_p$  method’.

Finally, some remarks should be made on the use of the extrapolation method for crystallinity determination. It is expected that the ‘extrapolation method’ described above will rapidly increase in popularity, for two reasons. In the first place the demand for quantitative DSC measurements will increase because, as



observed 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 can make the method suitable for any DSC user, regardless of the type of instrument used.

In conclusion, the 'extrapolation method' sketched above enables an analyst-independent determination of the crystallinity as a function of temperature in both cooling and heating. It is not necessary to perform heat capacity measurements, although it is of crucial importance that instrumental curvature of DSC curves has been eliminated via an empty sample pan correction. Experience has shown that due to the nature of the extrapolation (often across wide temperature ranges) and the nature of the calculation, see Eq. (A.3), this determination is extremely sensitive — not only to small differences in crystallization and melting but also to experimental imperfections. The best method is still a heat capacity measurement combined with an evaluation of the internal consistency of heat capacity and enthalpy data and a check with literature data (if available).

## Appendix B. Intermezzo II

### B.1. Metastability<sup>3</sup> and kinetics: reorganization, recrystallization and recovery

It is common practice among researchers to interpret a DSC melting curve and the associated characteristic quantities such as peak temperature in absolute terms, though it has been demonstrated many times that polymers exhibit a large degree of metastability, see [22,23] for recent discussions. The mere fact that perfect crystals with maximum dimensions in which the chains are extended (the kind of crystals one would expect on thermodynamic grounds) are obtained only under special conditions indicates that the crystallization process is far from ideal. For this reason, many researchers even prefer melting curves to crystallization curves; they reason that crystalliza-

tion is largely kinetically determined (because of the nucleation process), in contrast with melting. This idea is partly supported by the fact that melting does not require a nucleation process. On the other hand, it is a well-known fact that while crystallization curves are strongly influenced by the cooling rate, melting curves are heavily influenced by the cooling rate and the subsequent heating rate. In general, reorganization processes during heating are the rule rather than the exception. Only the degree to which they occur may vary; it is influenced by many factors, such as the thermal history, the temperature–time profile during heating and also the molecular structure.

An example of a standard evaluation performed with the aim of guiding processing operations is shown in Fig. 6 [24]. For various nylons, the crystallization peak temperature was measured as a function of cooling rate. A cooling rate change by two orders of magnitude results in considerable degrees of supercooling, up to tens of degrees. In some polymers, crystallization can even be prevented altogether by the application of extremely high cooling rates (by quenching in a suitable medium). This clearly illustrates that for polymers (molecular) nucleation [25] is

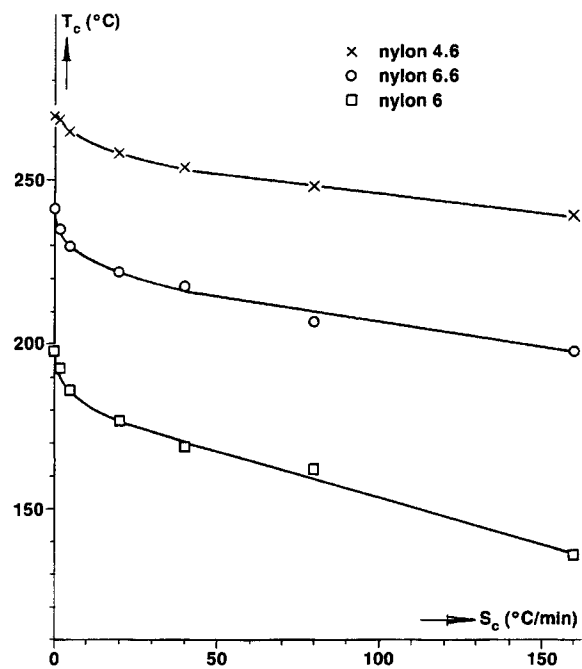


Fig. 6. Crystallization peak temperatures,  $T_c$ , for various nylons as a function of cooling rate,  $S_c$ .

<sup>3</sup>Partially derived from [22].

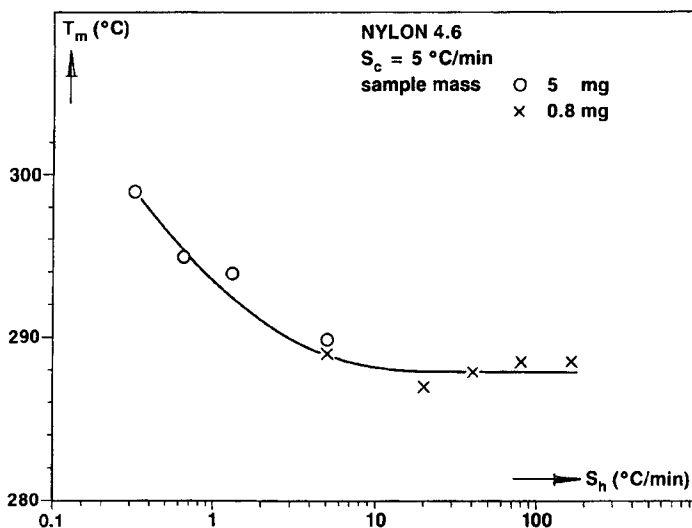


Fig. 7. Melting peak temperatures,  $T_m$ , for a nylon 4.6 as a function of heating rate,  $S_h$ .

a rate determining step in crystallization. It also illustrates that for these nylons DSC enables experiments to be performed on the time scale of nucleation and crystallization.

The resulting crystals will be metastable, especially if the growth rate of the metastable crystals exceeds that of the stable crystals. Still, there will virtually always be a tendency towards the thermodynamic equilibrium situation. In practice, this means that under conditions that tend to increase chain mobility, changes in morphology are likely to occur. Such reorganization processes occur more often than one would expect. Fig. 7 shows the heating-rate dependence of the melting peak temperature [24]. If the heating rate is increased 500-fold, the peak temperature decreases by  $10^\circ\text{C}$  before it becomes constant. We conclude that for this particular sample, with its particular thermal history (cooling at  $5^\circ\text{C/min}$ ), reorganization occurs at heating rates of  $5^\circ\text{C/min}$  and lower. The sample mass was chosen so as to minimize thermal lag and peak distortion.

Another well-known phenomenon observed during heating is recrystallization at a high temperature. When a polymer is rapidly cooled, for example, at  $160^\circ\text{C/min}$  as in the example of Fig. 6, or at much higher cooling rates during a processing operation such as injection molding or blown-film or cast-film production, moderately stable to unstable crystals are likely to be formed. During heating, these crystals may

reorganize as described above, but more often than not recrystallization will occur. In this process, the least stable crystals will melt wholly or partially during heating, then recrystallize into new crystals, and finally melt again as the material is heated further. Since recrystallization takes place at a temperature above the normal crystallization temperature, the crystals obtained are frequently more stable than the crystals obtainable in crystallization via cooling. As a result, melting takes place at relatively high temperatures. If the total peak area is determined, the total enthalpy of melting will hardly be influenced by recrystallization and melting, because the effects of (re)crystallization and remelting virtually cancel one another.

Fig. 8 illustrates the great capabilities of the scanning adiabatic (thin foil) calorimeter [26–28] applied to a metallocene-produced ethylene-1-alkene copolymer (probably 1-octene, density of  $900 \text{ kg/m}^3$ ). If the scan rate is increased from  $0.16 \text{ K/s}$  (DSC) via 7 to  $20 \text{ K/s}$ , the melting curves are lowered with respect to their position on the temperature axis, reflecting the hindering of reorganization processes. At the highest scan rate, the melting peak and melting end temperatures are lowered by approximately  $10^\circ\text{C}$  compared to the DSC curve.

In Fig. 9, the lower curve is a heating curve of a nylon 4.6 sample after rapid cooling. This gives a characteristic double-peaked heating curve which is

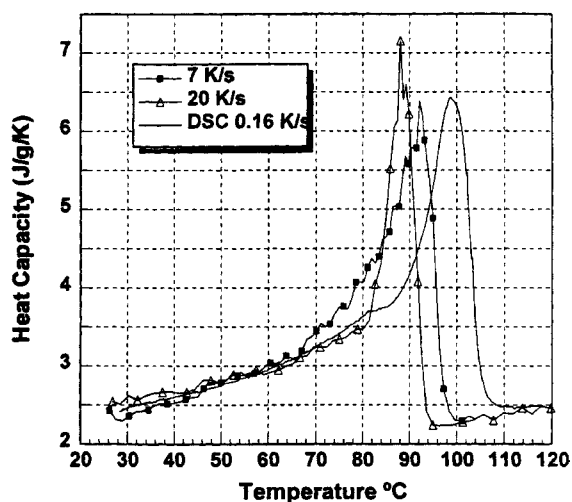


Fig. 8. Specific heat capacity curves of a metallocene ethylene-1-alkene copolymer using a fast scanning adiabatic (thin foil) calorimeter after natural-convection cooling from 120°C.

the net result of melting around 283°C (first endothermic peak) accompanied by recrystallization (exothermic) and subsequent remelting around 291°C (second endothermic peak). The method usually applied to show that the presence of two peaks is due to recrystallization and to prevent this recrystallization is,

again, variation of the heating rate. The higher the heating rate, the more effectively recrystallization is prevented, as is revealed by the fact that in the heating curve the first peak increases at the expense of the second, to the point where, in the ideal case, the second peak vanishes.

A striking example of recrystallization was observed during a DSC and real-time SAXS study of homogeneous ethylene-1-octene copolymers during heating at 10°C/min after quenching. A first set of the two samples was cooled at 0.1°C/min from 150°C (S samples) and a second set was quenched from the same temperature into liquid nitrogen (Q samples). These experiments were conducted to elucidate the higher DSC melting peak temperature for the Q samples compared to the S samples (Fig. 10A) and secondly to find out why the crystallinity of a Q sample overtakes that of the corresponding S sample during heating (Fig. 10B) [29–31]. The volume crystallinity was calculated from the mass fraction crystallinity [14] using temperature dependent densities of the reference states [32].

Firstly, a higher DSC melting peak temperature is found for the quenched samples, see Fig. 10A. During slow cooling (S samples), crystals are formed by a process of fractionation according to sequence length.

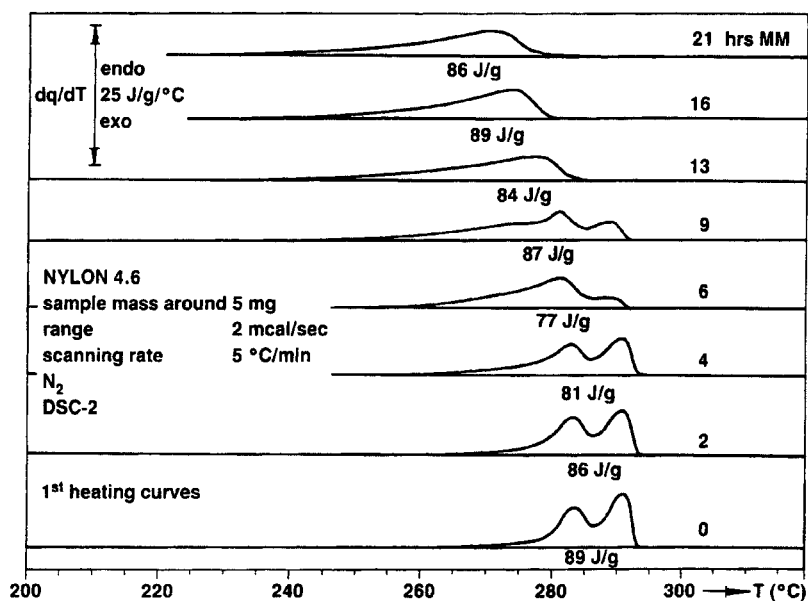


Fig. 9. First heating curves for the same nylon 4.6 as in Fig. 7. For each (new) sample, the duration in hours of the methoxymethylation treatment has been indicated.

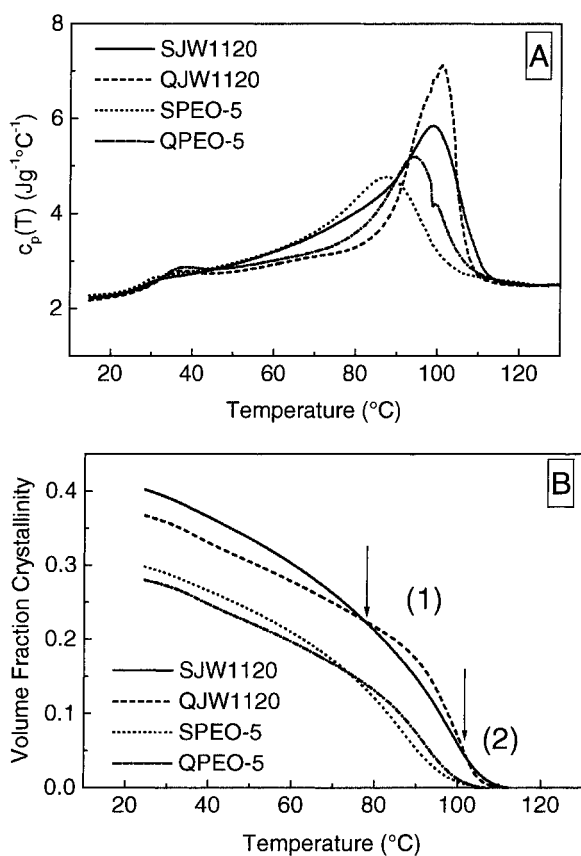


Fig. 10. DSC heating curves for two ethylene-1-octene copolymers: JW1120 and PEO5 with 5.2 and 5.5 mole% of octene and  $M_w$ s of 30,800 and 345,000 (g/mol), respectively. (A)  $c_p(T)$  values during heating; (B) volume fraction crystallinity obtained from DSC.

During subsequent heating, all crystals melt in the reversed order of their formation. DSC shows a broad endothermic signal, and the crystallite thickness,  $\langle T_c \rangle$ , increases because of the selective full strand melting of thinner crystals.

During quenching crystallization occurs at a much higher degree of supercooling than in the S mode. Sequences of different length cocrystallize as relatively thin, imperfect and unstable but uniform crystals. If the quenched samples are heated, the unstable (co)crystals melt upon the slightest increase in temperature. Nearly all ethylene sequences are released at the same time and recrystallization follows instantaneously since the temperature is relatively low and consequently the degree of supercooling is high.

These new crystals are still rather imperfect and there is considerable cocrystallization. The shortest sequences, released from the original crystals, no longer participate in this crystallization because of the higher temperature. At slightly higher temperatures these new crystals melt once again, and again most of the sequences are released. During subsequent recrystallization, slightly longer sequences are excluded as well. This process of melting and recrystallization repeats itself until crystals are formed that melt at such a high temperature that recrystallization is no longer possible during the time allowed in the heating process. Crystallization at high temperatures is slowed down because of a lower degree of supercooling and secondly because sufficiently long ethylene sequences are becoming scarce. The endothermic DSC signal partially overlaps with the exothermic signal of recrystallizing material, resulting in a narrow melting region and a peak at a relatively high temperature, i.e. higher than in the case of a slow cooling process. Clearly, the melting peak temperature of copolymers cannot be used to estimate the perfection or thickness of the crystals formed during cooling.

Secondly, DSC reveals a higher crystallinity for quenched samples in a particular temperature window during heating; see the region labeled (1) in Fig. 10B. Similar to DSC, the overall SAXS crystallinity of QJW1120 exceeds the crystallinity of SJW1120 during heating, while the results for PEO-5 are similar. Besides a minimum ethylene sequence length for crystallization at a given temperature, a minimum number of refolding chains is needed in order to avoid a density conflict: in the case of copolymers, overcrowding [33–35] of leaving chains may occur because hexyl branches are expelled from the crystal [36]. According to Vonk [34], at least 60% of the stems reaching the surface of a PE crystal have to bend back into the crystal of origin. For this reason, a number of the ethylene sequences which have the critical length for nucleation at a given temperature (but which are only a few times this length) are nevertheless expelled and do not participate in the crystallization. Such sequences can, however, crystallize at that specific temperature, provided they cocrystallize with longer sequences. The latter are able to crystallize with a re-entry loop, giving rise to a lower number of leaving chains at the crystal surface (i.e. overcrowding is avoided).

In conclusion, the lamellar crystals of slowly cooled homogeneous copolymers melt in the reversed order of their formation, which means that the thinnest crystals melt first. Quenching creates unstable crystals due to the cocrystallization of ethylene sequences with different lengths. These crystals repeatedly melt and recrystallize during heating. The exothermic heat due to recrystallization partially compensates for the endothermic heat due to melting, resulting in a narrow overall DSC melting peak with little overall endothermic heat development at low temperatures. This melting peak has its maximum at a temperature higher than the melting peak of slowly cooled copolymers. The lamellar thickness values of slowly cooled copolymers are always higher than those of quenched samples: i.e. the melting peak temperature cannot simply be linked to the melting of a dominant crystal population formed during previous cooling. The crystallinity of quenched copolymers overtakes the crystallinity of slowly cooled samples due to cocrystallization, which prevents overcrowding.

In some cases reorganization processes proceed so rapidly that even the above-mentioned scan rates are too low [37] to study, e.g., recrystallization in detail, let alone to prevent this process. A partial solution is provided by the scanning adiabatic calorimeter, see Fig. 8.

Another — but generally rather laborious — method for avoiding recrystallization is fixation of chains through cross-linking of molecules in the amorphous phase. Fig. 9 shows the use of a different method, viz. prevention of recrystallization by methoxymethylation [38]. The purpose of this treatment is to restrict the mobility of molecules by chemical cross-linking of the amorphous phase. Gamma irradiation of the samples in gaseous acetylene might also be used for this purpose [39,40]. In Fig. 9, it can be seen that the second melting peak indeed disappears when the duration of the treatment is sufficiently long. Complications arise if not only the amorphous phase but also the least stable crystallites or the crystal surfaces are attacked. This example shows that DSC can also yield insight into the effects of treatment methods like these.

Fig. 11 shows a large number of factors that influence the crystallization and melting behavior of LPE fractions with narrow molar mass distributions [41]. First of all it is clear that chain length is an important

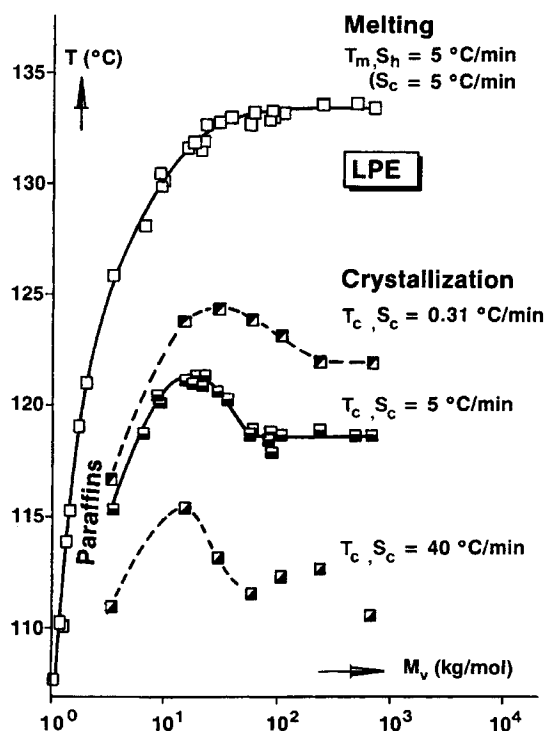


Fig. 11. Crystallization and melting peak temperatures,  $T_c$  and  $T_m$ , respectively, for linear polyethylene (LPE) fractions with narrow molar mass distributions, as obtained from DSC cooling and heating curves (sample masses of  $0.800 \pm 0.025$  mg), and  $T_m$  for paraffins, as obtained from the literature, as functions of molar mass. Influence of cooling rate on  $T_c$ .

parameter which, however, is often neglected or underestimated. At a cooling rate of  $5^\circ\text{C}/\text{min}$ , crystallization is increasingly hindered as the chain length increases, due to entanglements which prevent reptation of chain parts to the growth front. This causes the decrease in crystallization peak temperature with increasing chain length from approximately 20 kg/mol onwards. In the case of the smallest chains, crystallization and crystal growth still fall within Regime I [42], but from approximately 10 kg/mol onwards nucleation and crystal growth fall within Regime II. From about 100 kg/mol onwards, the peak temperatures are constant. This is because, on account of multiple nucleation (Regime III [43]), parts of the same chain are trapped in different crystal growth fronts (in the same crystal or in different crystals) so that the total chain length is no longer relevant. Incidentally, despite this constant crystallization

temperature the degree of supercooling still increases because the melting temperature still increases slightly with increasing chain length. At lower cooling rates, there is less hindrance with increasing chain length. Since there is more time available for disentanglement, crystallization takes place at higher temperatures, that is, at lower degrees of supercooling. As a result, multiple nucleation is also reduced: there is a shift towards nucleation and growth in Regimes I and II. Upon an increase in cooling rate the reverse occurs: a shift to higher degrees of supercooling and to Regime III nucleation and growth. It is interesting to note that crystallization apparently takes place on a time scale corresponding to that of the DSC conditions.

However, the development of the melting peak temperatures with increasing chain length is at least as interesting. An increase in  $T_m$  with increasing  $M$  is what everybody expects, but there is no relationship whatsoever with the development of  $T_c$ . Few people know this, because they usually study only the melting behavior and, although they do give a thermal history, fail to record the associated crystallization behavior. It will be clear from Fig. 11 that somewhere between cooling and heating reorganization occurs on such a scale that the expected relationship between  $T_c$  and  $T_m$  is completely obscured.

Obviously, this has many consequences. For one thing, it is not to be expected a priori that any meaningful relationships will be found between  $T_c$ , the morphology at room temperature and  $T_m$ . This means that Hoffman–Weeks [44] and Gibbs–Thomson [45] extrapolations will be impossible or very difficult because the crystal thickness is unlikely to be constant and therefore not unambiguously related to the  $T_m$  measured.

A final example illustrating the great potential of DSC in polymer research is the use of DSC for measuring the glass transition in a thermodynamically sound way, taking into account the kinetics of vitrification and devitrification. Fig. 12 shows a heating curve ( $20^\circ\text{C}/\text{min}$ ) for a polycarbonate previously cooled at  $0.1^\circ\text{C}/\text{min}$  [46]. A procedure has been developed for correctly determining the glass transition temperature,  $T_g$ , which characterizes the vitrification process (during cooling), from a heating curve [47]. Unfortunately, this procedure is still not widely used. The procedures used instead can have disastrous consequences and can even lead to wrong, contradictory conclusions as illustrated by Figs. 12–14 [46]. Using commercially available software packages, it is possible to determine characteristic quantities of a glass transition curve, as shown in Fig. 12: an ‘onset’ temperature; the temperature at which half of the total

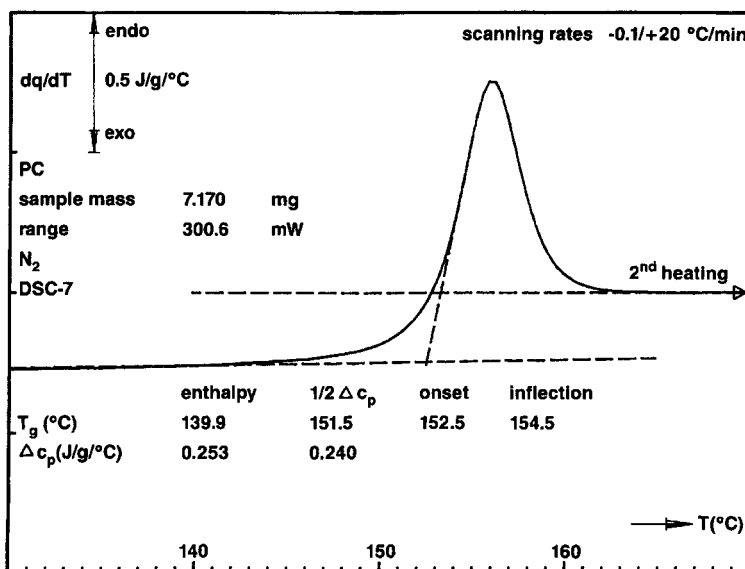


Fig. 12. Second heating curve of a polycarbonate at  $20^\circ\text{C}/\text{min}$  after cooling at  $0.1^\circ\text{C}/\text{min}$ . Different ways to establish a  $T_g$ .

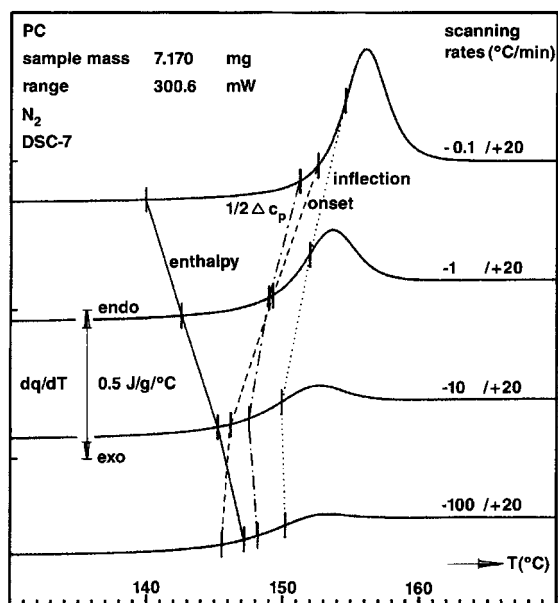


Fig. 13. Second heating curves of a polycarbonate, after cooling at various rates. Locations of  $T_g$  as calculated in different ways according to the preceding figure.

$c_p$  jump (moving from below the glass transition temperature to above this temperature) can be determined, referred to as  $(1/2)\Delta c_p$ ; the temperature of inflection, etc. With the aid of such quantities, the

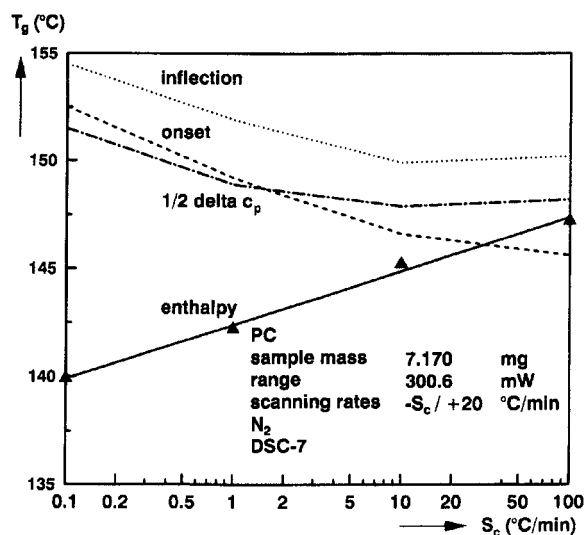


Fig. 14.  $T_g$  from the heating curves, as calculated in different ways in the preceding figure, at  $20^\circ\text{C}/\text{min}$  after cooling at  $S_c$ , as a function of the cooling rate.

devitrification process can be charted quite well. Some software packages additionally offer the possibility of determining the 'fictive' temperature, based on the 'enthalpy method' [47]. This temperature alone determines the 'intrinsic' glass transition temperature of the sample which is realized during cooling and which would be measured by a DSC instrument if the cooling curves were recorded. Obviously, this is not always possible, either because the cooling rate is too high to be imitated in a DSC instrument, as is the case with several processing methods, or because one has to measure the sample 'as such' without knowing its thermal history. This glass transition temperature realized during cooling is of course not affected by heating in the DSC instrument. On the other hand, the way the sample takes up enthalpy — the 'enthalpy recovery' — as reflected in the shape of the heating curve as a function of temperature, is strongly influenced by the heating rate, see Fig. 13. This figure shows heating curves ( $20^\circ\text{C}/\text{min}$ ) for a polycarbonate previously cooled at different rates, ranging from 0.1 to  $100^\circ\text{C}/\text{min}$ . Using the enthalpy method, it is possible to determine the glass transition temperature and thus gain insight into the thermal history regardless of the way the sample is heated. The method is described in detail in [47]. The result is shown in both figures. For thermodynamic reasons, it is to be expected that the glass transition temperature increases with increasing cooling rate, and this trend is reflected only in the fictive temperature. All other characteristic temperatures show the opposite (i.e. wrong) trend: they suggest that  $T_g$  decreases as the cooling rate increases! So if these temperatures are used as a basis for determining the glass transition temperature during cooling, they lead to wrong conclusions, as a result of which a research project may be steered in the wrong direction. It is obvious that the enthalpy method should be used, if only to enable comparisons with results obtained by other techniques. Finally, Fig. 14 presents an overview and shows the expected linear relationship between  $T_g$ , the glass transition temperature in cooling as determined by the enthalpy method, and  $S_c$ , the cooling rate during vitrification. It should be noted that curves such as the ones in Fig. 14 do provide insight into the expected dependency of devitrification (including the 'enthalpy recovery') on the thermal history, which means they provide information about the stability of the sample that is useful in practice.

From the above, the reader may have gained the impression that DSC results are to a large extent determined by the kinetics of the process studied and that it is apparently very difficult to obtain meaningful results unless special precautions are taken. Admittedly, a researcher who lacks a sound knowledge of the above-mentioned phenomena will easily interpret the results in the wrong way, the more so as DSC is very user-friendly, which suggests that it is a simple technique. However, it will also be clear from the above that DSC is an extremely powerful technique because it enables measurements to be carried out under dynamic conditions and makes it possible to obtain a clear picture of the metastability of polymers by offering a great variety of time–temperature programs.

### Appendix C. Intermezzo III

#### C.1. Real-time morphology measurements

As a first example we present real-time small angle laser light scattering (SALLS) measurements [48] on a (15/85 m/m) blend of an linear polyethylene (LPE) and a homogeneous ethylene copolymer with 5.2 mole% 1-octene, during cooling and subsequent heating at 10°C/min between 40 and 200°C.

The SALLS pattern was measured using a CCD camera to record Hv (polarizer and analyzer perpendicular) and Vv (polarizer and analyzer parallel) scattering patterns every 6 s during the temperature–time programs, corresponding to one pattern per °C in the temperature ramp. An averaged pattern of the melt was subtracted as a background and the relative total light scattering intensity,  $Q$ , of each pattern was obtained by integrating over both the scattering angle,  $\theta$ , and the azimuthal angle,  $\mu$  ( $Q_{Hv}$  and  $Q_{Vv}$  for a Hv and Vv experiment, respectively). In the case of space filling spherulites,  $Q_{Vv}$  is proportional to  $Q_{Hv}$ . The SALLS invariants were normalized with their value at 40°C assuming space filling spherulites at that temperature. All values of  $Q_{Vv}/Q_{Vv}^{(40^\circ\text{C})}$  are identical to those of  $Q_{Hv}/Q_{Hv}^{(40^\circ\text{C})}$  at temperatures where the spherulite volume fraction,  $\phi_{sp}$ , equals 1. At temperatures where  $\phi_{sp}$  is smaller than 1,  $Q_{Vv}/Q_{Vv}^{(40^\circ\text{C})}$  is larger than  $Q_{Hv}/Q_{Hv}^{(40^\circ\text{C})}$ , as is the case during, e.g., spherulite growth.

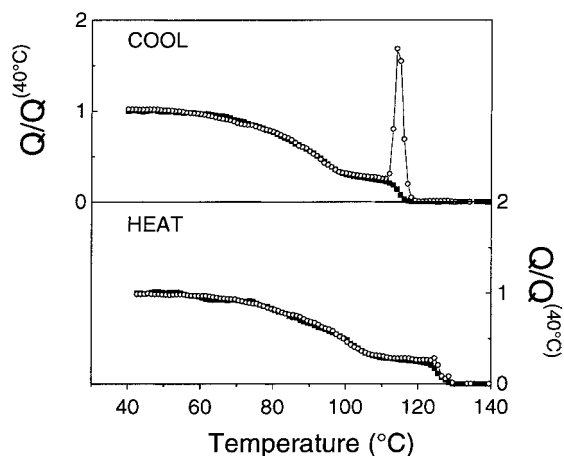


Fig. 15. SALLS: (full squares)  $Q_{Hv}/Q_{Hv}^{(40^\circ\text{C})}$  and (open circles)  $Q_{Vv}/Q_{Vv}^{(40^\circ\text{C})}$  during cooling and subsequent heating at 10°C/min between 200 and 40°C.

The SALLS invariant ratios are displayed for a cooling and subsequent heating experiment in Fig. 15. The differences in crystallization and melting behavior between the copolymer molecules (giving rise to the changes at lower temperatures) and the LPE molecules (responsible for changes at higher temperatures) in the blend are clearly seen from the resulting two-step behavior in both cooling and heating. This is also in line with the DSC results. Only at the highest temperatures during cooling, between approximately 110 and 120°C in the figure, is there a marked difference between  $Q_{Vv}/Q_{Vv}^{(40^\circ\text{C})}$  and  $Q_{Hv}/Q_{Hv}^{(40^\circ\text{C})}$ . At these temperatures primary crystallization takes place and the spherulites are not space filling. At lower temperatures, the morphology is obviously homogeneous on a  $\mu\text{m}$  scale. The spherulite diameter after cooling at 10°C/min is approximately 50  $\mu\text{m}$ . Though some excess in  $Q_{Vv}/Q_{Vv}^{(40^\circ\text{C})}$  is seen at the highest temperatures during heating, melting is fairly homogeneous (on a  $\mu\text{m}$  scale!) over the spherulite internal volume. Amorphous regions generated after copolymer melting are thus evenly spread over the spherulite volume and are so small that they cannot be detected by SALLS.

In order to obtain information on a sub-micrometer scale, real-time (synchrotron) SAXS (small angle X-ray scattering) measurements were performed using the same temperature–time program as the one used for SALLS. The results show that after the spherulites



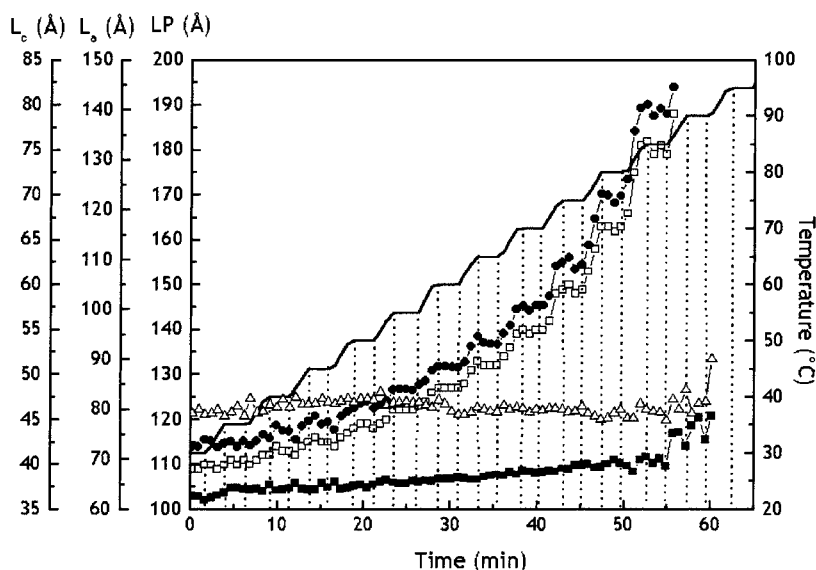


Fig. 16. LP ( $\square$ ),  $L_a$  ( $\bullet$ ) and  $L_c$  ( $\blacksquare$ ) of EB 2 quenched from the melt during a scan-iso heating run; ( $\triangle$ )  $L_c$  of EB 2 previously cooled at  $1^\circ\text{C}/\text{min}$ ; (—) temperature.

have become space filling during the primary crystallization (below approximately  $110^\circ\text{C}$ ), only 50% of the spherulite internal volume is occupied by semi-crystalline regions. Obviously, the spherulites are fairly open. During secondary crystallization, below approximately  $100$ – $110^\circ\text{C}$ , the amorphous regions inside the spherulites are gradually transformed into semi-crystalline regions as the remaining LPE molecules and the copolymer fraction crystallize. Below  $80^\circ\text{C}$  the crystals are homogeneously spread over the volume, and the increase in crystallinity inside the semi-crystalline regions due to further copolymer crystallization is very slight.

As a second example we present real-time X-ray measurements which provide a background to TMDSC measurements to elucidate complicated melting and crystallization processes in polymers [49–51]. The present real-time (synchrotron) small-angle X-ray scattering (SAXS) data were collected to monitor structural changes in a metallocene-based ethylene-1-butene copolymer with 6.4 mole% 1-butene (EB 2), using a ‘scan-iso’ temperature–time program [52]. Such a program should be regarded as an ‘underlying’ temperature–time program for performing TMDSC experiments (usually by superimposing a periodical temperature–time perturbation).

Copolymer EB 2 crystallizes in a spherulitic superstructure having a lamellar base morphology. Linear correlation functions could, therefore, be calculated and analyzed to obtain the long period, LP, the amorphous layer thickness,  $L_a$ , the crystalline layer thickness,  $L_c$ , and the local volume fraction crystallinity in the semi-crystalline regions.

The influence of the scan-iso heating program on LP,  $L_a$  and  $L_c$ , is shown in Fig. 16 for EB 2, quenched from the melt and previously cooled at  $1^\circ\text{C}/\text{min}$ . LP and  $L_a$  follow the scan-iso temperature–time profile rather closely: they increase during the heating segments and remain more or less constant during the isothermal stays. LP and  $L_a$  of quenched EB 2 increase from 109 to  $188\text{ \AA}$  and from 73 to  $145\text{ \AA}$ , respectively.  $L_c$  of the quenched sample increases slightly; this may be due to the melting and recrystallization of the imperfect lamellae into thicker ones, even approaching the values for the slowly cooled sample at high temperatures. By contrast, in the case of the slowly cooled sample there is hardly any influence of the scan-iso heating program and its  $L_c$ -values are higher than those of the quenched sample at all temperatures. Also, no isothermal lamellar thickening is observed. Rearrangements within crystallites are unlikely to occur since the short chain branches hinder diffusion

of chains. Given the near constancy of  $L_c$ , the increase in LP must be due to the increase in  $L_a$ . The results show that for the homogeneous ethylene-1-butene copolymer studied, considerable structural changes occur within a few minutes during dynamic (heating) and static (isothermal) measurements. Obviously, in corresponding TMDSC experiments, important morphological parameters, such as LP,  $L_a$ , crystallinity, etc. do change as a result of the underlying temperature–time program. As a next step, it would be very interesting to study the changes in morphology as caused by the periodic perturbations themselves, for instance using real-time X-ray, SALLS, solid-state NMR, etc. The observations stress the importance of time-resolved measurements. Obviously, since the morphology of the sample changes during the measurement, static measurements are meaningless in this temperature range. Consequently, in TMDSC studies of crystallization and melting processes the temperature–time program, and especially the amplitude and the period of modulation, should be carefully chosen. Such TMDSC studies should preferably be complemented with real-time experiments to elucidate related morphological changes.

## Appendix D. Intermezzo IV

### D.1. Thermal diffusivity and conductivity

In industrial practice it is essential to have knowledge of the thermal properties of a material, e.g., its thermal conductivity. Especially in materials processing and in the engineering of products with certain desired properties it is necessary to have specific information available in combination with other parameters, such as heat capacity, density etc. For instance, in injection molding processes involving polymers it is of importance to set the temperature profiles as effectively as possible. However, thermal diffusivity/conductivity data are also needed for optimizing the economy of the process.

Usually, such information is not available, or only a rough indication can be found in the literature, mostly a single value relating to room temperature. What is needed, however, is information about the actual temperature range of relevance to the process used. In the case of polymers this range can be very wide, typically spanning 200 degrees. Quite often no rele-

vant data are available over such ranges, nor data relating to the regions below, in or above transition ranges such as crystallization and melting, devitrification and vitrification ranges. Since computer-aided design and computer-aided engineering (CAD–CAE) software increasingly needs temperature-dependent input data, it is important that these data be generated.

Common measurement procedures for getting such data are, however, difficult and tricky. This is the case even for samples having a simple shape such as disks or sheets, while measurements on complex shapes, for example, actual products, are barely feasible. Even results obtained on simple samples are often quite scattered and show contradictory trends as far as temperature dependence is concerned. This is due in part to the fact that the experimenters who generate the data are not familiar with the special features of polymeric materials or with the transitions studied. However, another, even more important reason is that hardly any commercial instrumentation is available for such investigations.

Another factor to be considered is that the morphology of the polymeric system influences not only the results but also the measuring method. Crystallinity is known to be an important parameter, while the dimensions and the packing of the crystallites in a semi-crystalline polymer are also important factors. Orientation on all scales (from nano to macro) of molecules (in both amorphous and semi-crystalline materials), crystallites and superstructures (in semi-crystalline materials) has a marked influence. However, few instruments are capable of handling these aspects. In processing, pressures up to approximately 500 MPa are possible, so it would be useful to be able to carry out measurements not only as a function of temperature but also as a function of pressure. In the special case of composite materials, diffusivity and conductivity are not additive, in contrast to various other properties, so they first need to be measured thoroughly. Only if reliable data are generated will it be possible to develop useful modeling and engineering techniques.

## Appendix E. Intermezzo V

### E.1. High-pressure DSC

Studies into the influence of pressure not only increase our basic understanding of the crystallization

and melting of polymers, but also generate basic practical knowledge of the final properties of materials produced under high-pressure processing conditions (e.g., injection molding).

There are only a limited number of polymers whose morphology has been studied at elevated pressures. Some thermal studies have been performed on polyethylenes, see [53] for an overview. However, results for homogeneous ethylene-1-alkene copolymers at elevated pressures (>100 MPa) have not been reported in the literature so far. To fill this gap, homogeneous ethylene-1-octene (EO) copolymers with relatively low comonomer contents have been investigated [54] at elevated pressures using X-ray and high-pressure DSC [55,56]. A linear polyethylene sample, LPE, as produced with the same vanadium-based catalyst as the EO copolymers, was included as a reference material.

It is a well-known fact that an increase in crystallization temperature, or annealing above the crystallization temperature of PE, may result in thicker folded-chain lamellae. The induced pressure can also lead to molecular constraints that inhibit the orthorhombic-melt transition during heating because the random coil conformation cannot be attained. At the same time, if the pressure increases, crystallization and melting occur at higher temperatures, where larger interchain distances (larger unit cell volume) and higher chain mobility allow the material to organize itself into a hexagonal phase or a CONDIS [57] type of phase. As a result, the chains have the opportunity to organize themselves into much thicker lamellae than usual-crystals can grow as much as several micrometers [58,59] in the chain axis direction — involving a decrease in the number of folds, or even into extended chain crystals (ECCs). ECCs are formed by crystallization from the melt into the hexagonal phase, whereas folded chain crystals (FCCs) are formed by crystallization from the melt into the orthorhombic phase. The studies of Rastogi et al. [60], using more precise optical microscopy and X-ray measurements at high pressures, favor the suggestion made by Bassett and Khalifa [59] that at pressures above 200 MPa crystal growth occurs only in the hexagonal phase (stable or metastable).

Since most of the interpretations and explanations of high-pressure phenomena described in the literature focus on linear and slightly branched polyethylenes

(LPE and HDPE), there is a need for new data on homogeneous ethylene-1-alkene copolymers with a higher degree of branching. Compared to LPE, the hexyl branches in copolymers hinder the crystallization process and the chain mobility in the resulting crystallites. This generally leads to a lower degree of crystallinity and to smaller and less perfect crystallites. In the case of ethylene-1-octene copolymers, the side branches moreover limit the thermodynamically favored chain extension in the crystallites during crystallization and during annealing. The chain mobility under high pressures will at best be high enough to enable chain sequences to extend to lengths comparable to the distance between the branching points, limiting the crystal thickness to values comparable to contiguous ethylene sequence lengths. Hence, in ethylene-1-octene copolymers this can lead at most to ‘extended ethylene sequence crystals (EESCs)’ instead of ‘extended chain crystals (ECCs)’ as in case of polymers without branches (LPE) or with very few short branches (HDPE).

In the heating curve at 550 MPa of the LPE, see Fig. 17a, three endothermic peaks are observed: a small low-temperature peak (I), a pronounced major peak (II) at an intermediate temperature and a smaller high-temperature peak (III). When the pressure is lowered, the peak temperature difference between Peak II and Peak III becomes smaller and the temperatures probably coincide at 425 MPa and lower. According to Hikosaka and Minomura [61] and Rastogi et al. [60], Peaks I, II and III should be assigned to the melting of orthorhombic FCCs, to the orthorhombic ECC → hexagonal ECC transition superposed on the melting of orthorhombic ECCs and to the melting of the hexagonal structures, respectively. The small low-temperature peak (I) can be detected at pressures above 400 MPa. Below this pressure, a broad endotherm is observed which is probably due to the merging of the different transitions mentioned before. Extrapolations from the peak temperatures to lower pressures support this possible superposition. As the pressure is lowered, the hexagonal peak (III) moves closer to Peak II and finally disappears, supporting the absolute necessity of high chain mobility for the occurrence of the hexagonal phase.

In the case of a low 1-octene content (2.1 mole%), too, a three-peak melting pattern is observed, see Fig. 17b, consisting of (probably): a small low-tem-

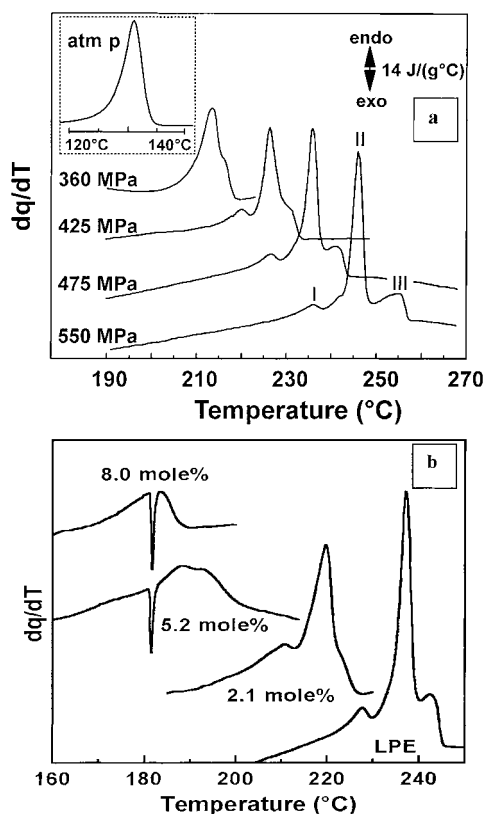


Fig. 17. (a) Heating curves after cooling of the LPE at different pressures; scan rate  $10^{\circ}\text{C}/\text{min}$ . (b) Heating curves after cooling of the LPE and the copolymers having different 1-octene contents at 475 MPa; scan rate  $10^{\circ}\text{C}/\text{min}$ .

perature melting peak of FCCs (I), a large melting peak of orthorhombic ECCs/EESCs, possibly superposed on the orthorhombic ECC/EESC  $\rightarrow$  hexagonal phase transition (II) and a high-temperature melting shoulder of the hexagonal phase (III).

With increasing 1-octene content, see Fig. 17b, the three-peak endothermic pattern at high pressure evolves over a broad two-peak pattern (probably only I and II, 5.2 mole% 1-octene) into one broad endotherm (probably only I, 8.0 mole% 1-octene). One can assume that in the 8.0 mole% copolymer, the chain mobility is so restricted that extension of the ethylene sequences and/or the appearance of the high-temperature/high-pressure hexagonal phase is hindered or absent. Therefore, the formation of FCCs with folded ethylene sequences is favored over ethylene sequence extension. Moreover, the mobility of

the chains is lower because, due to the high comonomer content, the transitions take place at lower temperatures.

In Fig. 18, the crystallization ( $T_c$ ) and melting ( $T_{m,I}$ ) peak temperatures (symbols) of the LPE sample and the three homogeneous ethylene-1-octene copolymers are plotted versus the comonomer content for the pressures applied. In reality, the transition peak of the samples is much broader than that of a pure compound; hence, there is a transition range rather than a specific transition temperature. The peak maximum is characteristic of the temperature of the maximum transition rate of the sample. Fig. 18 shows that upon an increase in pressure  $T_c$  and  $T_m$  shift to higher temperatures. This temperature increase is most pronounced at lower pressures. It follows from Fig. 18 that the way in which the melting peak temperature of FCCs varies as a function of the comonomer content is independent of the pressure, as reflected in the parallel curves. The decrease in  $T_c$  and  $T_m$  with increasing comonomer content is larger in the case of small amounts of 1-octene than in the case of higher amounts. The dotted lines in Fig. 18a and b are fitting curves. The equations found are obviously not optimal at atmospheric pressure, where  $T_c$  and  $T_{m,I}$  reveal a linear relationship with the comonomer content. Therefore, a straight line is drawn as well.

## Appendix F. Intermezzo VI

### F.1. Temperature Modulated Reaction Calorimetry

Reaction calorimetry is widely regarded as a powerful tool for the development, scale-up and optimization of chemical processes and for safety studies relating to these processes. Key features of this technique are full process control (i.e. working under real plant conditions) and the possibility to determine heat transfer coefficients (UA) and the specific heat capacity of a system ( $c_p$ ).

However, in cases in which the heat economy of a chemical process cannot be derived from the heat balance of the reactor due to a lack of knowledge of heat transfer and heat capacity changes during the reaction, it is almost impossible to obtain accurate quantitative data for such a process using commercially available software modules. Especially in cases

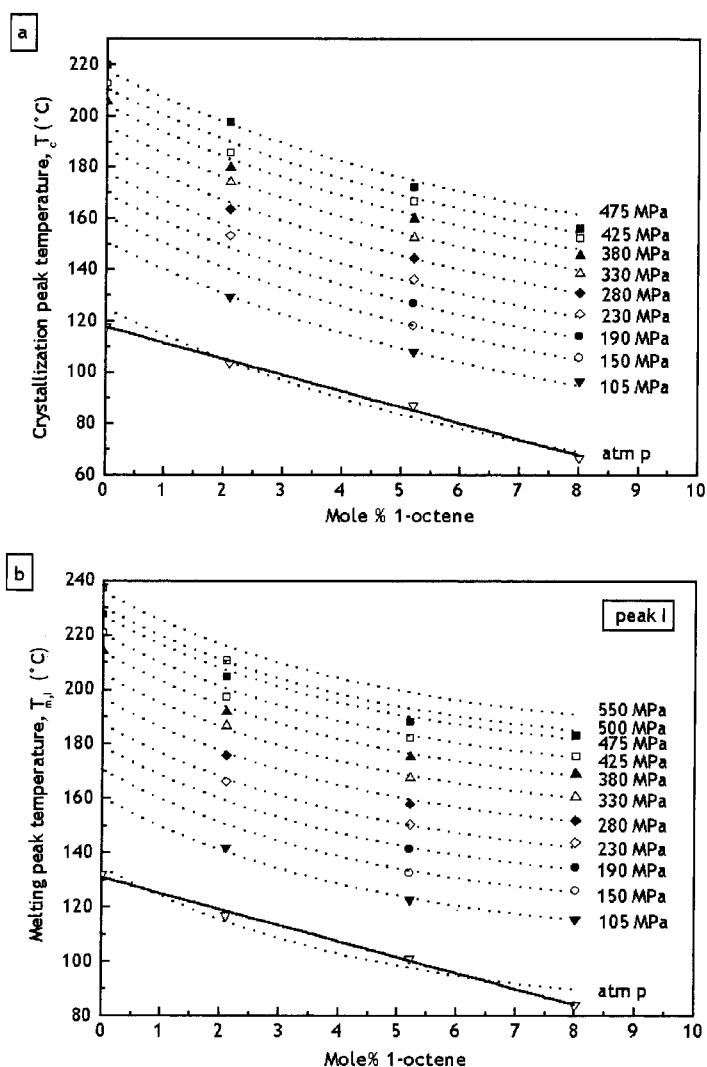


Fig. 18. Crystallization (a) and melting (b). Peak I temperatures in cooling and subsequent heating, respectively, at  $10^\circ\text{C}/\text{min}$  as a function of the 1-octene content at different elevated pressures; dotted lines in (a) and (b) represent fitting curves.

where the heat transfer (and heat capacity) is affected by the reaction (e.g., viscosity increase, precipitation of products on the reactor wall, phase transitions etc.) heat transport through the reactor wall is greatly hindered, which can lead to a runaway reaction if the cooling capacity of the reactor fails. The consequences of a runaway reaction in a chemical plant can be catastrophic. Therefore, there is an urgent need for more detailed measurements of UA and  $c_p$  during the reaction.

Recently, Carloff et al. [62] have developed a special reaction calorimeter to fill this need for on-line  $c_p$  and UA determinations. In this apparatus, the so-called temperature oscillation reaction calorimeter (BOCAL), a sinusoidal temperature modulation is applied to the reactor jacket. Temperature modulated techniques not only provide the same information as conventional calorimetric techniques but also permit the analysis of complex processes by, among other things, determining the change in the heat transfer

coefficient during a reaction from the associated modulating heat flow. The advantage of this approach over the conventional method has been demonstrated successfully on various high viscosity systems (e.g., solution polymerization of methylmethacrylate). Despite its benefits, the BOCAL is not commercially available.

Currently, a commonly used commercially available reaction calorimeter is the RC-1 instrument from Mettler–Toledo. Its possibilities with regard to, e.g., the dosing of reactants, pH measurement and control, IR-sensors, etc. make this calorimeter a very versatile tool in chemical process studies.

A recent innovation by Baldo et al. [63] involves the modification of the standard RC-1 equipment (TMRC-1) in such way that a modulated temperature profile can be programmed. A block temperature profile is induced in the reactor, resulting in a modulated heat flow. Analysis of this heat flow signal allows the on-line determination of variations in UA and  $c_p$ , independently from each other. In this way the overall heat of reaction can be determined in a more accurate way compared with the conventional calculation, where a linear interpolation of UA and  $c_p$  values between start and end times of the reaction is assumed to be applicable, or even worse, constant values have to be taken. Even if start and end times of the reaction are available, interpolations are quite unreliable because the actual path depends in an unknown way on various parameters, such as the set-up of the reactor, stirring devices, the degree of fouling etc.

The benefits of using this temperature modulated approach are nicely demonstrated in a calorimetric study of the radical polymerization of methylmethacrylate in solution [63]. The polymerization process follows the classical kinetic scheme for a free radical polymerization reaction with a first order overall reaction constant. One of the characteristics of this polymerization is the gradual increase in the viscosity of the reacting mixture during the highly exothermic reaction. The heat transfer and specific heat capacity are so strongly affected by this viscosity increase that they eventually become unknown quantities, preventing a full evaluation. In such a case one is forced to use constant UA and  $c_p$  values.

Fig. 19a shows the results obtained for the polymerization of methylmethacrylate in ethyl acetate while applying a quasi-isothermal block temperature

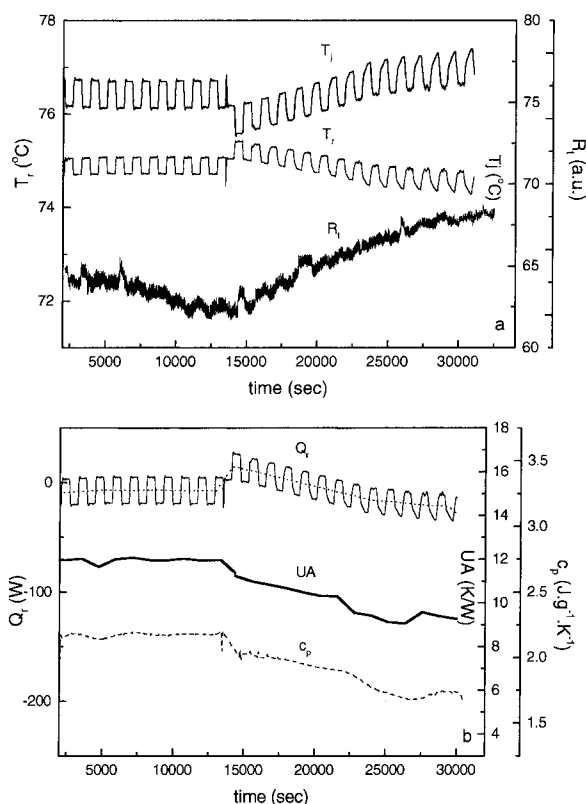


Fig. 19. (a) Radical polymerization of methylmethacrylate in ethylacetate studied in a quasi-isothermal mode with TMRC-1. A block temperature profile was induced in the reactor with an amplitude of  $0.2^{\circ}\text{C}$  and a period of 20 min. The temperature in the reactor ( $T_r$ ), the jacket temperature of the reactor ( $T_j$ ) and the torque of the stirrer ( $R_t$ ) were monitored during the experiment. At  $t=13,000$  s, polymerization was initiated by the addition of AIBN; (b) Calculated values of the heat flow of reaction ( $Q_r$ ), the heat transfer coefficient (UA) and the specific heat capacity ( $c_p$ ) during the polymerization based on the raw data presented in Fig. 1a (exotherm is plotted upwards).

profile to the reactor (2 l, glass). The quasi-isothermal temperature ( $T_r$ ) was set at  $75^{\circ}\text{C}$  with a modulation period of 20 min and an amplitude of  $0.2^{\circ}\text{C}$ . The temperature difference between the reactor contents ( $T_r$ ) and the reactor's jacket temperature ( $T_j$ ) were recorded as a measure of the heat flow ( $Q_r=UA(T_r-T_j)$ ) under isothermal conditions, assuming no other heat loss factors. The viscosity of the reaction mixture was measured via the torque of the stirrer ( $R_t$ ). After 10 modulation cycles ( $t=13,000$  s), polymerization was started by the addition of the radical initiator (2,2'-azo-bis-isobutyronitrile). Immediately after the

initiation, an exothermic heat flow ( $Q_r$ ) was observed, accompanied by a strong viscosity increase ( $R_t$ ).

Fig. 19b shows the on-line UA and  $c_p$  values that were calculated from the modulated temperature profiles displayed in Fig. 19a. Clearly, a decrease in UA is observed as a consequence of the hindered heat transport through the reactor wall caused by the increasing viscosity. The  $c_p$  decreases analogously due to the changing chemical nature of the system. This insight into the on-line changes in  $c_p$  and UA is essential in safety studies and in the development and scaling-up of processes.

Using these actual values of  $c_p$  and UA, the exothermic heat of polymerization is determined (leading to  $\Delta h = -203$  J/g MMA) in a much more realistic manner than according to the conventional method. Due to the increasing viscosity (as caused by solidification of the reaction mass, severe fouling of the reactor after completion of the reaction, etc.), the conventional method fails because no  $c_p$  and/or UA determinations can be performed during and after the reaction. If the  $c_p$  and UA values before the reaction are assumed to hold during and after the reaction, the result is  $\Delta h = -240$  J/g MMA.

In general, conventional operation of the RC-1 can lead to incorrect determinations of the heat of reaction, resulting in either underestimated or overestimated values. Both cases can have major consequences: an underestimation leads to unsafe operations, whereas an overestimation might induce unnecessary financial investments in, e.g., pressure relief systems or quench vessels in the reactor.

## Appendix G. Intermezzo VII

### G.1. Three-phase models needed

As mentioned in Intermezzo I, for many polymers the well-known two-phase model offers a useful first-order description of the morphology.

However, 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 observed deviations 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 [14]. 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 like the one described here be used by the thermal-analysis and calorimetry community. Therefore, TA&C software should become available which supports two- and three-phase models.

## Appendix H. Intermezzo VIII

In this connection, it is useful to draw a comparison with the situation at many large companies. Most of them are still aware of the need to maintain state of the art analytical expertise, as a precondition for effective research. Some companies have maintained a central facility which the various company units can turn to for support in the field of methods and techniques, see Section 2.1. Such a facility — which is in fact the company's expertise center — should be given the necessary financial resources for carrying out fundamental research so as to be able to keep abreast of developments, translate these developments to its own situation and develop its own methods and techniques. In addition, such a group should act as an intermediary in cases where certain specialist measurements are outsourced because it would be impossible or impracticable to carry them out in-house. This outsourcing happens more often than many people think. Companies are likely to become increasingly critical in deciding which activities should be retained in-house and which activities should be outsourced. They are also increasingly willing to contract out certain measurements to universities (under a secrecy agreement, of course). More and more companies are considering the possibility of sharing expensive analytical equipment with other companies. There is no reason why these companies should not be willing to use the services of external expertise centers if these can offer the required know-how and are sufficiently business-

like in their approach. The latter requirement can sometimes lead to tension but this is mostly a question of mentality on the part of the researchers involved. So it would seem logical that expertise centers at universities as described above maintain contacts not only with the scientific community but also with the 'expertise centers' of industrial companies.

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