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THE USE OF DIFFERENTIAL SCANNING CALORIMETRY IN CHEMICAL EDUCATION
II. A graduate experiment, the melting behaviour of ultra-high molecular weight polyethylene fiber

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An overview is given of the potential of DSC in chemical education, both in the undergraduate and in the graduate phase.

The way in which the introduction of DSC in chemical education is facilitated, is outlined. A comprehensive description is given of a graduate experiment, the melting behaviour of ultra-high molecular weight polyethylene fiber.

It is shown that, using such an experiment, various chemical and physical processes in substances can be easily demonstrated.

Keywords: chemical education, DSC,polyethylene

Introduction

Thermal analysis techniques belong to the most rapidly growing analytical tools. In particular, Differential Scanning Calorimetry nowadays constitutes a very important and frequently used technique in almost every laboratory.

It is therefore of paramount importance that thermal analysis in all its aspects forms integral part of the curriculum of education institutes, irrespective of their location in the world.

The present situation, however, is still far from perfect, mainly as a result of two impeding factors:

1. the absence of well-suited instrumentation
2. the absence of special educational tools, allowing a rapid introduction of thermal analysis , without a demand for intensive teacher effort.

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The first factor was eliminated by the development of the DSC12E, introduced by Mettler in the beginning of 1991. A comprehensive description of this instrument and its background philosophy can be found in references [1, 2].

The second factor was eliminated by the compilation of the 'Proficient Pac' [3]. This instructional aid consists of the following parts:

1. A textbook, entitled 'The practice of Thermal Analysis' [4]. This book, divided into two parts, first describes the backgrounds of the various thermal analysis techniques and their applications in chemistry and physics. Thereafter, in Part 2, a comprehensive description is given of 16 very illustrative experiments which can be performed by the individual student in a limited amount of time. An overview of these experiments is given in reference [5].

2. A set of 35 overhead- and projector slides clearly describing the basics of the various thermal analysis techniques.

3. A poster summarizing the basics of DSC.

Next to the Proficient Pac, a sample kit [6] is available containing most of the samples needed to perform the experiments described in 'The Practice of Thermal Analysis'.

In the first part of this series [5], a description was given of an undergraduate experiment, the dehydration of coppersulphate. It was shown there that even with such a rather simple and straightforward experiment much insight can be gained by the student on various chemical and physical phenomena.

Here, attention is given to a graduate experiment, the melting behaviour of ultra-high molecular weight polyethylene fiber.

Experimental

All experiments have been carried out using the Mettler DSC12E differential scanning calorimetry. Use was made of sample #11 of the educational sample kit, the Dyneema SK60 fiber produced by DSM.

A description of the experiment

Ultra-high molecular weight polyethylene fibers belong to the class of ultra strong materials. They feature tensile strengths of more than 6 GPa and moduli >160 GPa [7].

This performance is due to the high degree of molecular orientation within the fiber. As a result, both the enthalpy ΔH_{sl} and the entropy of melting ΔS_{sl} differ considerably from the randomly configured isotropic polyethylene. Due to the melting condition $\Delta G_{sl}=0$, these fibers show a very complex melting behaviour.

In order to gain insight into the large differences between the melting behaviour of the fiber and the 'normal', isotropic polyethylene and the extensive transformations which occur on molecular level during melting, in a first experiment a sample is heated up to a temperature of 170°C, cooled down to 100°C and reheated up to 170°C. The resulting curves are given in Fig. 1.

The very large differences between the first and the second heating curve (A and C) result from orientational effects only. In fact, the second heating curve represents the melting curve of normal HDPE. In this way, the influences of ΔH_{sl} and ΔS_{sl} on the melting temperatures can be very nicely illustrated.

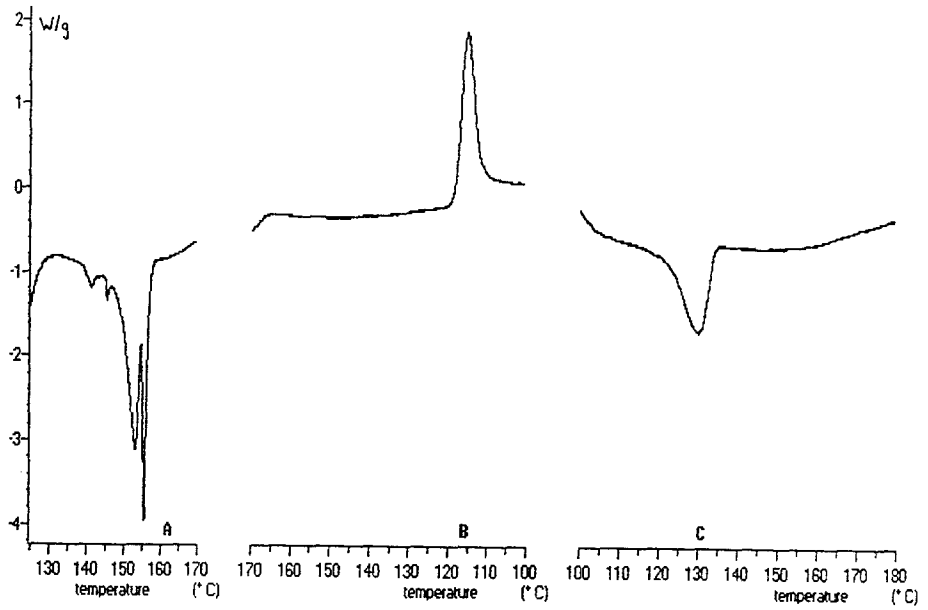

Fig. 1 Melting and crystallization curve of UHMWPE (5 deg/min) A First melting, B Cooling, C Second melting

Secondly, the influences of experimental parameters on the measured curve are to be determined. It can be clearly shown that significant measurements should be performed with very small sample weights. In Fig. 2 the

measured curves are compared of a sample with a weight of 0.4 mg (A) and a sample with a weight of 3.5 mg (B)(both normalized to the same scale). As the time constant of the DSC12E is small [5], these differences are only due to the sample weight, leading to the conclusion that for these types of samples the sample weight should be very small. In general, it was concluded that the product of sample weight in mg and the heating rate in deg/min should be less than 2 (this means that many results presented in the literature should be treated with caution).

Especially for fibers, the influence of sample preparation on the measured curve is large. As to that, Fig. 3 compares the melting curve of small (4 mm) filaments (A) with that of the fiber tied to a knot (B). The very distinct differences between those two curves completely result from extra stress built up in the knot during heating, leading to peaks at temperatures up to 160°C.

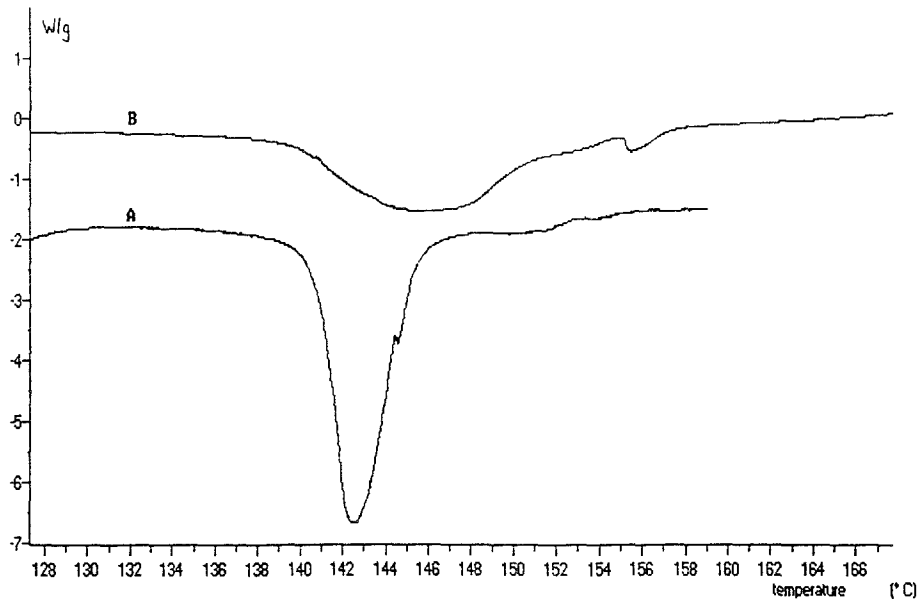

Fig. 2 The influence of sample weight on the melting curve (5 deg/min) A 0.4 mg, B 3.5 mg

The behaviour of one single filament of the fiber is interesting in this respect. Thanks to the high sensitivity of the DSC12E it was possible to measure one filament with a length of 5 mm and a weight of 0.001 mg. Here, the filament was folded into a small piece of aluminium foil, which was placed directly onto the sensor. The resulting curve given in Fig. 4 shows a

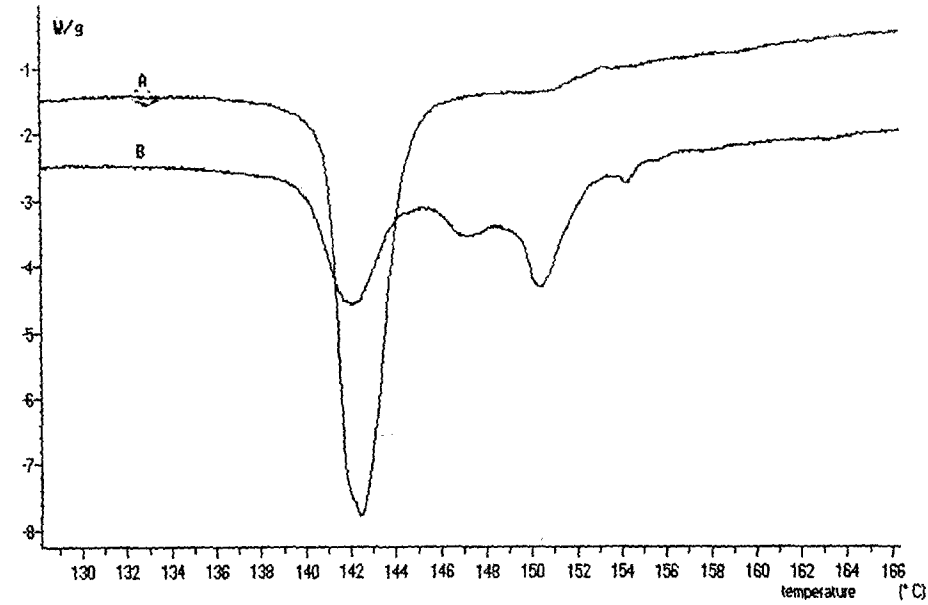

Fig. 3 The influence of fiber shape on the melting curve (5 deg/min) A Linear filaments 4 mm, B Knot

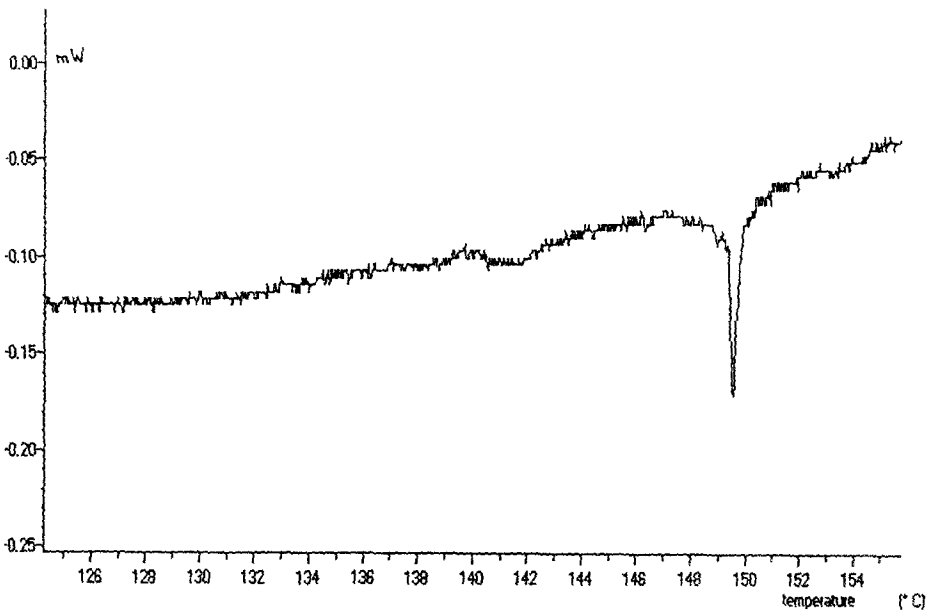

Fig. 4 The melting curve of 0.001 mg fiber (5 deg/min)

hardly visible endothermic effect at approx. 142°C, belonging to the part of the filament being able to shrink freely. The main part melts at approx. 149°C due to the extra stress resulting from the jamming in the aluminium foil.

In this way, the students not only gain clear insight into the great influences of sample preparation on the measured curves, but also into the way external variables may influence the melting curve. In this respect, it is interesting to make the students perform some investigations towards the nature of the high temperature peaks in Fig. 3B. Hereto, a sample tied to a knot is heated up to 152°C and cooled down directly. The cooling curve then (Fig. 5B) shows two exotherms, the first at approx. 147°C, the second at approx. 122°C. Obviously, the latter is the crystallization peak of the part molten at 142°C. Heating again (Fig. 5C) it gives a peak at approx. 130°C (the melting temperature of isotropic polyethylene) and two sharp endotherms at 152 and 154°C. By repeated heating-cooling cycles, up to 152°C; this pattern does not change, leading to conclusion that the peak at 152°C is due to a solid-solid phase transformation instead of melting (in fact this is the orthorhombic to hexagonal transformation). In this way, many experiences are obtained about possible processes which take place at higher temperatures.

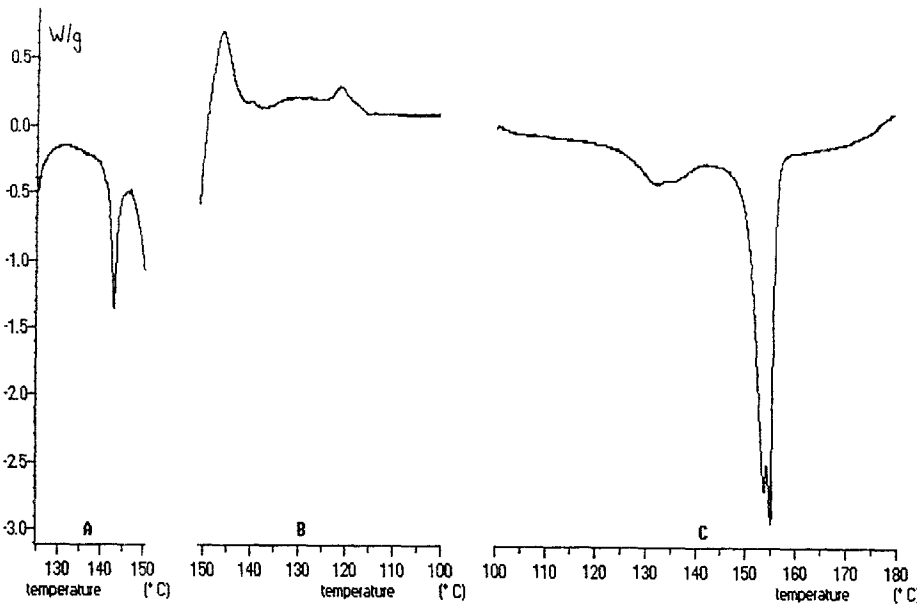

Fig. 5 Solid-solid phase transformations of polyethylene A First heating, B Cooling, C Second heating

Finally, using this sample, relaxation phenomena can be studied nicely. Thereto, the sample is heated up to 142°C (the melting temperature of the oriented phase), kept isothermally during various times, cooled down to 100°C and reheated. Characteristic curves are given in Fig. 6.

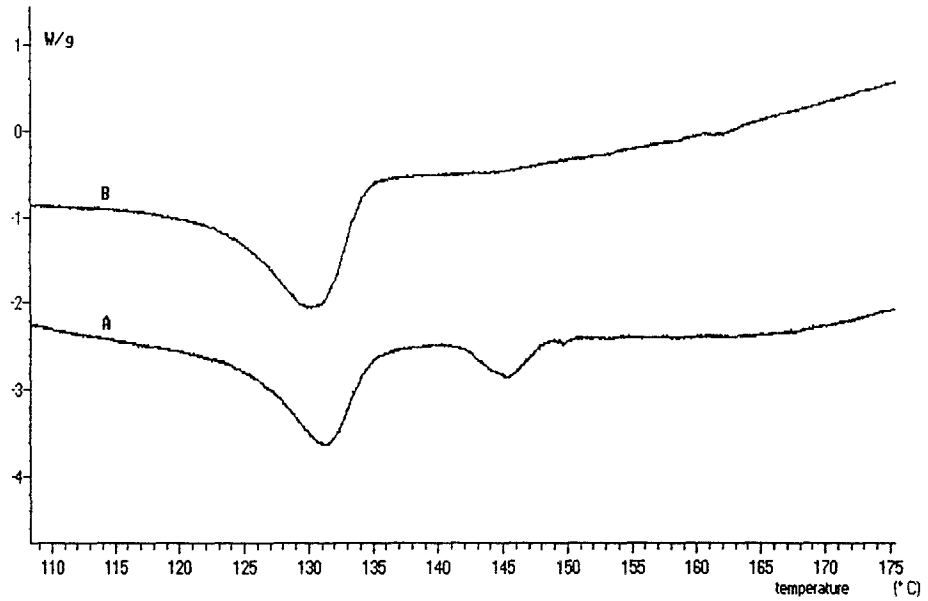

Fig. 6 Relaxation processes in the oriented phase A 5 min isotherm at 142°C, B 25 min isotherm at 142°C

It can be clearly shown that relaxation processes proceed slowly, as a result of the very large molecular chains involved. Comparing this with relaxation processes of substances with low molecular weight gives much information on the molecular movements involved.

Conclusions

As a result of their special molecular orientation, fibers form samples with a very high 'educational value'. Reactions on molecular level are clearly represented into the DSC curves, again illustrating the high information content of this very powerful analytical technique. The rather simple and rapid experiments described here give the student a good insight into many chemical and physical processes taking place in the sample. Of course, the

experiments reported here just serve as an example and can easily be extended by the individual teacher.

References

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Zusammenfassung — Es wird ein Überblick über die Leistungsfähigkeit von DSC in der Chemieausbildung, sowohl in der Hochschul- als auch in der Postgraduate-Phase vermittelt. Es wird ein Weg aufgezeigt, wie die Einführung von DSC in der Chemieausbildung erleichtert werden kann. Die ausführliche Beschreibung eines Hochschulexperimentes, das Schmelzverhalten von ultrahochmolekularem Polyethylenfiber wird gegeben.
Es wird gezeigt, daß derartige Experimente geeignet sind, verschiedene chemische und physikalische Vorgänge leicht demonstrieren zu können.