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HEAT CAPACITY, ENTHALPY AND CRYSTALLINITY FOR A LINEAR POLYETHYLENE OBTAINED BY DSC

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By means of computer-controlled DSC, heat-capacity measurements were performed on NBS SRM 1484 between – 70°C and 250°C, in heating as well as cooling. By using stepwise and continuous measuring methods together with enthalpy calculations, an insight was obtained into the intrinsic consistency and the accuracy of the measurements. The reference states of polyethylene within the two-phase model were used to determine the crystallinity as a function of temperature, and to evaluate various other methods employed for the same purpose.

For many years the DSC technique has been generally used in the thermal analysis of materials. Computerization has enlarged the possibilities of control and data manipulation, so that not only have measurements and evaluation been speeded up, but accuracy has increased as well. Meanwhile the point has been reached where accuracy is no longer restricted by peripheral apparatus, but only by the calorimeter itself. This will be illustrated with reference to c_p measurements on polyethylene.

Although polyethylene has long been a subject of study [1, 2], hardly any quantitative measurements are known for the interval from room temperature through the whole of the melting range, the very area to which by far the greater part of the present calorimetric studies relate, and, indeed, the area in which c_p and crystallinity show strong changes.

This article presents findings in the range from – 70° to 250°, measured by stepwise and continuous methods, which give a good idea of what can nowadays be achieved with commercial equipment. The c_p values are used to calculate enthalpy values, whilst also the crystallinity is calculated as a function of temperature and the findings are compared with those of various other methods of calculation used for the same purpose.

The results are discussed within the framework given by the so-called reference states of purely amorphous and purely crystalline polyethylene [2].

Experimental

Use was made in the measurements of a Perkin—Elmer DSC-2 arranged on-line with a Tektronix 4052, a Hewlett—Packard 3495A scanner-multiplexer, and an HP 3455A digital voltmeter (5½–6½ digit). The measuring interval was 0.2 K. The temperature calibration was done by means of indium, the energy calibration by means of Al_2O_3. For weighing, use was made of a Mettler ME 22/36 electronic microbalance.

Measurements were performed on the linear polyethylene NBS SRM 1484 [$M_n = 91$, $M_w = 121$, $M_z = 154$ (kg/mol) according to GPC] supplied by the U.S. Dept. of Comm. Nat. Bureau of Standards, Washington.

Results and discussion

Figure 1 shows $c_p(T)$ curves determined in cooling as well as in heating. The c_p values are positive, both in cooling ($dQ < 0$, $dT < 0$) and in heating ($dQ > 0$, $dT > 0$), but in conformity with normal usage the exothermic ($dQ < 0$, $dt > 0$) processes are represented by a downward, the endothermic ($dQ > 0$, $dt > 0$) processes by an upward curve.

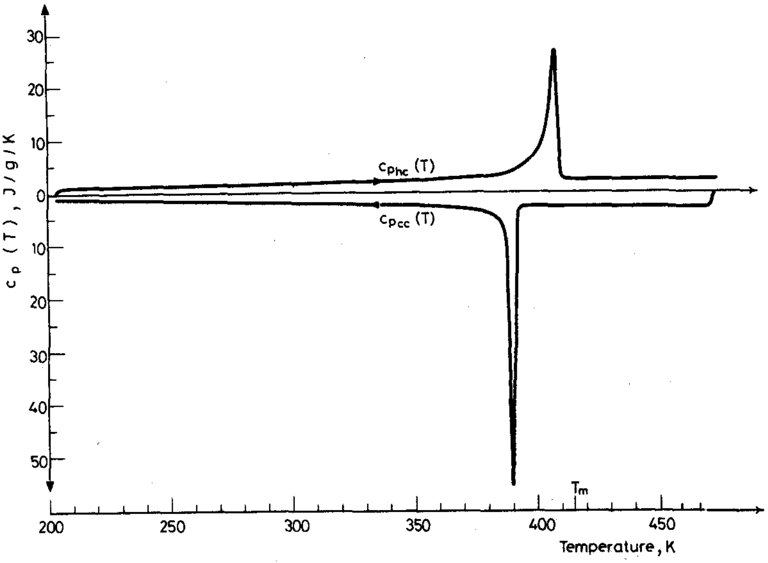

Fig. 1 The DSC cooling and heating curves for the linear polyethylene NBS SRM 1484, measured by the continuous c_p method. Peak temperatures 389.4 K and 407.0 K. Sample weight: 4.320 mg, range: 1 mcal/sec, scanning rate: ±10 degree/min, isothermal stays at 473 K and 203 K: 5 min, N_2: 20 cm^3/min

Use was made of the continuous c_p method [3–8], i.e. measurement on sample plus pan and analogously on the empty pan in one run through the whole temperature range, which in this particular case spanned 270 degrees. The c_p measurements show crystallization followed by melting of the sample, with, as is known for this type of dynamic measurements, the peak shape being determined largely by thermal history and sample weight.

We will start our discussion with an estimate of the weight percentage crystallinity, w^c, from the area under the peak, made in the usual way. The best procedure to obtain the required base line is extrapolation from the melt data, which results in peak areas for the heating curve (indicated by hc) and the cooling curve (cc); the respective areas are indicated by $A_{1,\mathrm{hc}}$ and $A_{1,\mathrm{cc}}$. Usually, such transition enthalpies are divided by $\Delta h(T_m) = 293$ J/g. *In this case we thus get:*

$$w^c_{\mathrm{hc}} = \frac{A_{1,\mathrm{hc}}}{293} \cdot 100 = \frac{177.5}{293} \cdot 100 = 61\% \tag{1}$$

and, in the same way:

$$w^c_{\mathrm{cc}} = 60\% \tag{2}$$

$A_{1,\mathrm{hc}}$ is the peak area over the connecting line $c_{p_{\mathrm{hc}}}(350) \Leftrightarrow c_{p_{\mathrm{hc}}}(415)$, $A_{1,\mathrm{cc}}$ the area over $c_{p_{\mathrm{cc}}}(340) \Leftrightarrow c_{p_{\mathrm{cc}}}(400)$.

However, a crystallinity determination as described above is known to be inadequate, for several reasons. In the first place, the crystallinity values obtained in this way are related to the temperatures corresponding to the points of intersection between the base lines and the curves – $T^*_{\mathrm{hc}} = 350$ K and $T^*_{\mathrm{cc}} = 340$ K in this case – and are hence dependent on the shape of the curve [4–7]. Further, instead of $\Delta h(T_m)$ the value $\Delta h(T^*)$ should be used, as has been explained at length in [2], and has, indeed, long been recognized and practised [4–7, 9–14].

Eqs (1) and (2) should, consequently be changed to

$$w^c_{\mathrm{hc}}(350) = \frac{A_{1,\mathrm{hc},350}}{\Delta h(350)} \cdot 100 = \frac{177.5}{279} \cdot 100 = 64\% \tag{3}$$

and, analogously:

$$w^c_{\mathrm{cc}}(340) = 64\% \tag{4}$$

However, these values are als unsuitable for making a comparison with results obtained by other methods, e.g. density, X-ray, Raman measurements, etc., as such comparisons mostly require the use of the value of the crystallinity at room temperature. This value can be obtained by extrapolating from the melt data to room temperature along a straight line and decreasing the peak area A_1 by the area A_2 comprised between the extrapolation line and the c_p curve under the point of intersection T^*. For NBS SRM 1484 we thus get:

$$w^c_{hc}(300) = \frac{[A_1 - A_2]_{hc,300}}{\Delta h(300)} \cdot 100 = \frac{166.6}{251} \cdot 100 = 66\% \tag{5}$$

and, in the same way:

$$w^c_{cc}(300) = 67\% \tag{6}$$

(For the definition of $[A_1 - A_2]_T$, see Fig. 2.) In the same way the function $w^c(T)$ can be determined for any other temperature by extrapolation from melt data, taking into account the temperature dependence of Δh. According to [2], $\Delta h(T)$ is very adequately described by $\Delta h(T)_M$, which is a function that is easy to use when $T \geqslant 290$ K. On this basis we have, in Fig. 2, shown $w^c_{hc}(T)$ and $w^c_{cc}(T)$ calculated by means of

$$w^c(T) = \frac{[A_1 - A_2]_T}{\Delta h(T)_M} \cdot 100\% \tag{7}$$

with

$$\Delta h(T)_M = 293 - 0.3092 \cdot 10^{-5}(414.6 - T)^2(414.6 + 2T) \text{ J/g} \tag{8}$$

The method of determination outlined above is simple in application if there are possibilities for data aquisition and manipulation, and can be used for ordinary DSC (non-c_p) curves as well.

The above does not yet provide much insight into the internal consistency and the accuracy of the measurements. This requires a more extensive evaluation of the c_p measurements and, in addition, the performance of enthalpy calculations. Figure 3 shows the same measurements on a scale that is ten times more sensitive. We here see small details, e.g. around 360 K, the small peak in the cooling curve that is often found for polymers containing ethylene. The figure further contains the classical stepwise measurements [8, 14–17] which were performed with 32 K intervals and isothermal stays of 5 minutes. This measuring method cannot be used if during the isothermal stays thermal processes take place, as is the case here at the peaks. We see that outside the peak areas there is surprisingly good agreement with the continuous c_p measurements. Our experience has shown combination of these two measuring methods to be essential if a good idea of the reliability of the measurements is to be obtained.

As appears from the figure, the cooling and heating curves are symmetrical with respect to the temperature axis (apart from the peaks), which inspires confidence in the measurements from a thermodynamic viewpoint. It should be remarked here that c_p values measured in cooling are really scarce, although such measurements are at least equally important as the usual c_p measurements made in heating. Also, combination of the two types of values in principle provides a possibility to test the degree of thermodynamic irreversibility during the measuring procedure [18].

Besides points of agreement there are also points of difference between the two types of measurement themselves as well as with respect to the reference curves. These reference curves $c_{p_a}(T)$ and $c_{p_c}(T)$ are the specific heat capacity curves for purely amorphous (index a) and purely crystalline (index c) polyethylene, respectively,

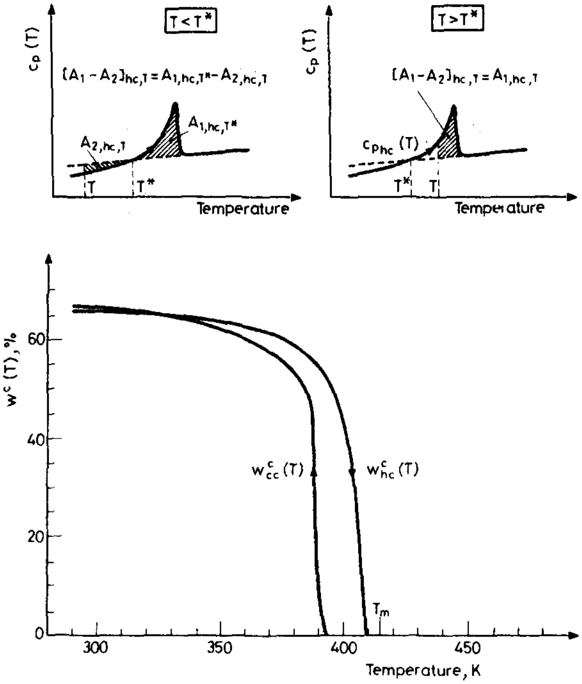

Fig. 2 $w^c(T)$ according to (7) in cooling and in heating. Inserts: definition of $[A_1 - A_2]_T$ for a heating curve (the same applies to a cooling curve)

as determined in [2] with assumption of the two-phase model. The differences appear from the continuous measurement in the melt for determination of the cooling curve, which systematically gives values that are too law in relation to $c_{p_a}(T)$, and are observed also at low T for both curves. These deviations are bound up in part with problems typically encountered in measurements on polyethylenes, and in part with the stability of the DSC, as will be explained in a separate publication. The inaccuracy of the c_p values at the lowest T is apparent also from the crystallinity calculated by means of c_p, which calculation is allowed because the crystallinity of the sample will be practically constant in this range:

$$w^c_{hc}(220) = \frac{c_{p_a}(220) - c_{p_{hc}}(220)}{c_{p_a}(220) - c_{p_c}(220)} \cdot 100 = \frac{1.54 - 1.27}{1.54 - 1.21} \cdot 100 = 82\% \qquad (9)$$

and analogously:

$$w^c_{cc}(220) = 88\% \qquad (10)$$

To make these too high crystallinity values agree with the results of enthalpy calculations, $c_p(220)$ needs to be increased by 0.06 J/g/K, which is admissible in view

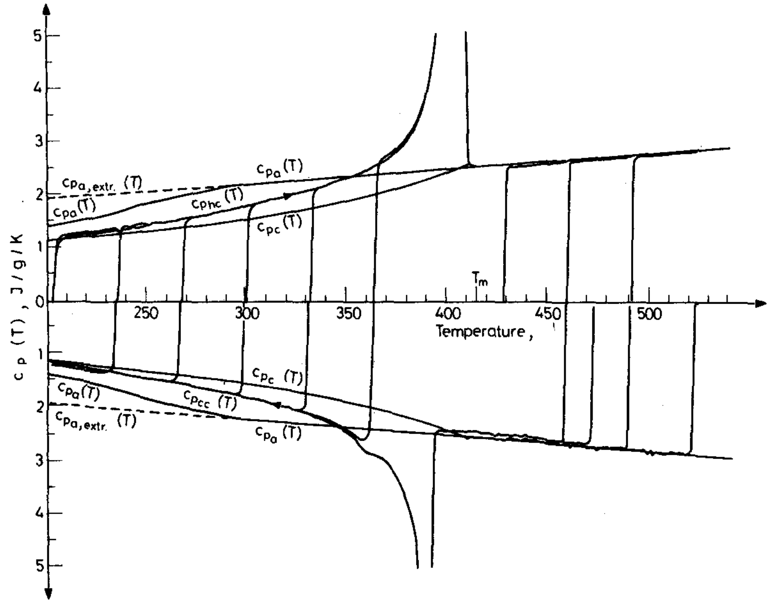

Fig. 3 The DSC cooling and heating curves as drawn from continuous and stepwise c_p measurements, and the reference curves. Sample weight: 4.320 mg, range: 1 mcal/sec, scanning rate: ± 10 degree/min, isothermal stays: 5 min, N_2: 20 cm^3/min. Temperature is in K.

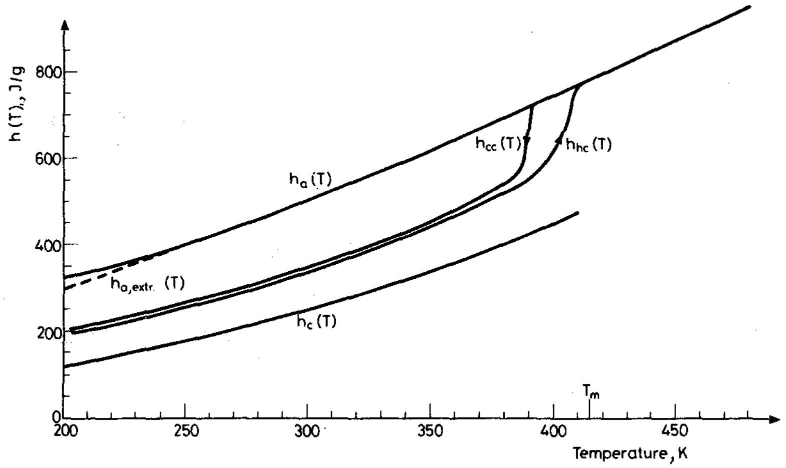

Fig. 4 Specific enthalpy curves calculated from the DSC measurements in combination with the reference curves

of the experimental error. This also makes it clear that the quality of the measurements is still insufficient to test the correctness of the extrapolation to c_{p_a} and c_{p_c} values described in [2].

Also shown in Fig. 3, by interrupted lines, is $c_{p_{a,\mathrm{extr.}}}(T)$, which is an extrapolation from data for the supercooled melt according to (51) in [2] and is indicated by * in Fig. 5 of that publication.

The too low c_p values of the cooling curve for the melt and partly also for the high-temperature side of the peak result in systematic deviations of $h_{cc}(T)$ with respect to $h_{hc}(T)$ for temperatures above and below the calibration point at $T_m =$ $= 414.6$ K in the enthalpy plot, Fig. 4. This is reflected also in Fig. 5 for $w^c_{cc}(T)$ with respect to $w^c_{hc}(T)$, both calculated by means of:

$$w^c(T) = \frac{h_a(T) - h(T)}{h_a(T) - h_c(T)} \cdot 100\% \tag{11}$$

At 300 K this result in:

$$w^c_{hc}(300) = \frac{h_a(300) - h(300)}{h_a(300) - h_c(300)} = \frac{167}{251} \cdot 100 = 67\% \tag{12}$$

and, similarly:

$$w^c_{cc}(300) = 63\% \tag{13}$$

The result according to (12) is in agreement with (5), beacuse the baseline virtually coincides with the line for $c_{p_a}(T)$, which implies that also the enthalpies derived from them show practically the same course. This is not so in the case of the cooling curve, hence the low value found according to (13). In the procedure followed for (6) there is a compensation for deviations, so that eventually the result is still reasonable. This is also evident from Figs 2 and 5.

Figure 5 shows that the crystallinity slightly decreases towards lower temperature; for the heating curve there is a decrease from 67% at 300 K to 65% at 220 K. Such a very small decrease has, indeed, been reported before [19, 20], but we think that in this particular case it may be caused by the c_p values being too low in this temperature range. An increase of c_p in the temperature range from about 200 K to 300 K by 0.06 J/g/K, for instance, causes the crystallinity at 220 K according to (11) to go up from 65% to 67%, whereas the crystallinity value based on c_p – see (9) and (10) – at the same time decreases substantially, from about 85% to the same end value of 67%.

Extrapolation from the data for the supercooled melt (interrupted lines in Fig. 5) results in an even stronger decrease of $w^c(T)$ towards low temperature. The crystallinity values as calculated according to [1] show better analogy.

Table 1 gives a survey of the crystallinities at three temperatures found by different methods of calculation. For the table and the figures, the $c_p(T)$ and $h(T)$ curves were calculated as follows: $c_{p_c}(T)$ was calculated by means of a polynomial fit of the values in [2], Table 4 (10 K – 410 K); $c_{p_a}(T)$ by means of a polynomial fit of the values

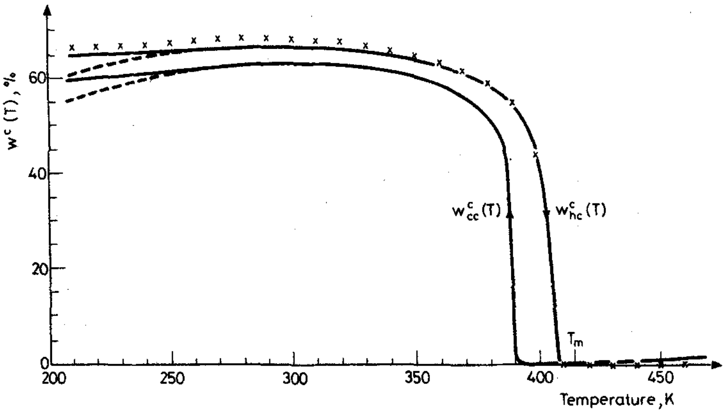

Fig. 5 $w^c(T)$ calculated from the DSC measurements according to (11): full lines. $w^c(T)$ according to method of calculation F in Table 1 (see also Fig. 4): interrupted lines. X: $w^c(T)$ according to [1] for the heating curve

Table 1 Crystallinities for the linear polyethylene NBS SRM 1484 based on c_p measurements, calculated by various methods

Methods of calculation				$w^c(T)$, %	
			220 K	300 K	350 K
A	$\frac{h_a(T)-h(T)}{\Delta h(T)}$	hc	65	67	64
		cc	61	63	61
B	$\frac{[A_1-A_2]_T}{\Delta h(T)}$	hc	–	66	64
		cc	–	67	63
C	$\frac{[A_1-A_2]_T}{\Delta h(T)_M}$	hc	–	66	64
		cc	–	67	63
D	$\frac{[A_1-A_2]_T}{293}$	hc	–	57	61 ①
		cc	–	57	60
E	$\frac{c_{pa}(T)-c_p(T)}{\Delta c_p(T)}$	hc	82	–	–
		cc	88	–	–
F	$\frac{h_{a,\mathrm{extr.}}(T)-h(T)}{h_{a,\mathrm{extr.}}(T)-h_c(T)}$	hc	63	As A	
		cc	58		
G	As A ②	hc	66	68	64

① As, for both hc and cc, $T^* \cong 350$ K, these values are equal to $[A_1]_{T^*} \cdot 100/293$ = peak area · 100/293.

② $h_a(T)$ and $h_c(T)$: tabular values according to [1], with $h(T)$ calibration at (414.6 K, 772 J/g).

in [2], Table 4 (10 K – 290 K), plus polynomial (51) in [2] for 290 K – 630 K; $h_c(T)$ from the c_{p_c} polynomial with calibration at (414.6 K, 486 J/g); $h_a(T)$ from the c_{p_a} polynomial with calibration at (414.6 K, 779 J/g) and (290 K, 485 J/g); and $h(T)$ from $c_p(T)$ by numerical integration (trapezoidal rule) and calibration at (414.6 K, 779 J/g).

As we have seen, method A yields good results here for the heating curve, albeit that at low temperature the crystallinity comes out slightly too low, probably because of the c_p values being on the low side. The same too low c_p values also cause the too high $w^c(T)$ values based on c_p (method E). The lower $w^c(T)$ values for the cooling curve (A) are due to the c_p values for the melt being too low. Extrapolation from melt data towards the desired temperature in combination with $\Delta h(T)$ (method B) gives correct crystallinity values. In the case of the cooling curve this means that there is a compensation for errors. If the discontinuity in $c_{p_a}(T)$ at 290 K, see [2], is accepted, the extrapolation should not be carried below 290 K. Above 290 K, $\Delta h(T)_M$ (see C) is a function that is a handy substitute for $\Delta h(T)$. A sure source of errors is failure to account for the temperature dependence of $\Delta h(T)$ (method D).

As will have become clear from the foregoing, the performance of both stepwise and continuous c_p measurements plus an overall analysis by the various calculatory methods is essential if a correct idea is to be formed of the quality of the measurements. The measurements reported here show that it is possible to perform within an acceptable time span c_p measurements and an evaluation using a commercially obtainable calorimeter with associated control and data-processing facilities. From our experience we conclude that the limiting factor as regards accuracy is the instability of the calorimeter during the measurements, with measurements on polyethylenes additionally bringing specific problems. Hence we would still regard these measurements as semi-quantitative, although they have a reasonable level of quality.

Improvement of the quality of the measurements by further optimization of the calorimeter is of importance notably for further refinement of the simple two-phase model [21–25]. Concrete problems needing to be solved here are, for instance, those posed by the inaccuracy of the c_p values at low temperature, as mentioned, and by the discrepancies in the extrapolation according to $w^c(T)$ to $c_{p_a}(T)$ and $c_{p_c}(T)$, as mentioned in [2].

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Zusammenfassung — Die Wärmekapazität von NBS SRM 1484 wurde im Temperaturbereich von – 70 bis 250°C durch komputer-kontrollierte DSC sowohl während der Aufheizung- als auch während der Abkühlung gemessen. Durch Anwendung schrittweiser und kontinuierlicher Messmethoden zusammen mit Enthalpieberechnungen wurde ein Einblick in die innere Konsistenz und die Genauigkeit der Messungen gewonnen. Die Referenzzustände von Polyäthylen in dem Zweiphasenmodell wurden zur Bestimmung der Kristallinität in Abhängigkeit von der Temperatur und zur Bewertung verschiedener anderer, zum gleichen Zwecke angewandter Methoden herangezogen.

Резюме — С помощью ДСК, контролируемого ЭВМ, выполнены измерения теплоемкости для образца НБС СРМ 1484 между – 70°С и 250°С как при нагреве, так и охлаждении. Путем использования ступенчатого и непрерывного метода измереный, совместно с вычислениями энтальпии, удалось проникнуть во внутреннюю последовательность и точность измерений. Эталонные состояния полиэтилена в пределах двухфазной модели были взяты для определения кристалличности в зависимости от температуры, а также для оценки других различных методов, используемых для той же самой цели.