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POLYMER CRYSTALLINITY DETERMINATIONS BY DSC*

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ABSTRACT

Differential scanning calorimetry (DSC) and quantitative differential thermal analysis (DTA) are widely used to determine the crystallinity of semicrystalline polymers according to the so-called "calorimetric method". The procedure involves the determination of the heat of fusion of the polymer sample which is usually determined by measurement of the area of the melting peak above a somewhat arbitrarily interpolated baseline. In many cases the results depend strongly on the operator's estimate of the "correct" baseline position.

In other cases crystallization and recrystallization effects during the heating but prior to melting render baseline methods fundamentally unsound. The theory of the calorimetric method is applied to DSC data to show that simple baseline interpolation is rarely permissible in polymer heat of fusion measurements, and a generally applicable procedure is suggested which involves the measurement of the total energy absorbed in the melting region.

INTRODUCTION

For a variety of practical reasons, it is customary to think of the solid state of a "semicrystalline" polymer as being composed of x weight fraction crystalline material and $(1-x)$ weight fraction amorphous material. Although it is now well known that this so-called "two-phase" model is an inadequate description of the morphology of such polymers and that the size distribution, perfection, orientation, and nature of the surfaces of the crystalline regions strongly influence the polymer's properties; the parameter, x, is nevertheless a broadly useful number in the routine characterization of polymer samples. At least to the extent that the two-phase model is a fair representation of a polymer's morphology, the value of x should be a fair representation of its "crystallinity." We find that the density or specific volume of semicrystalline polymers varies between the limits of that of a perfectly crystalline and a perfectly noncrystalline sample; that the IR spectra exhibit "amorphous" and

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"crystalline" absorption bands; that NMR detects both relatively immobile or "crystalline" chains and floppy or "amorphous" chains; and that X-ray diffraction patterns show both highly ordered and highly disordered regions of reasonable size[1,2]. Thus even though the finer details of the polymer morphology are important, most actual physical measurements are interpretable in terms of the two-phase model. When analyzed quantitatively, they also yield values of x which correlate well with gross physical properties of the materials. Sometimes, several different methods applied to the same sample yield nearly the same value of x[3,4], further lending credence to its interpretation as the "crystallinity".

Unfortunately, none of the methods for crystallinity determination can be considered as giving an absolute answer; and they all involve uncertainties or assumptions in the data analyses. When two different methods fail to give the same answer, it is difficult to determine if the two methods really measure different "kinds" of crystallinity or whether there were simply errors in the experiments or methods of data analysis. Since we can potentially learn a good deal about the morphology of semicrystalline polymers by comparing the results of several different experimental approaches[5,6], it is important that we critically evaluate our methods and eliminate as much uncertainty and subjectivity as possible.

A method of determining the crystallinity of polymers which has become particularly popular in recent years is based upon the measurement of heats of fusion by DSC[5-7]. The theory of the method derives from the pioneering work of Dole[8,9] and coworkers who published a series of papers which illustrated the broad utility of calorimetry in characterizing polymer morphology and thermal behavior. Experimentally, however, the DSC method more closely resembles the DTA approach which was first applied extensively to polymer studies by Ke[10]. DSC may be thought of as combining the quantitative capability of conventional calorimetry with the speed, convenience, and microsampling capability of DTA[11].

Because early DTA studies were at best semiquantitative in nature, little attention was paid to the detailed method of analyzing the melting peak to obtain the heat of fusion. It is customary in both DTA and DSC to draw what appears to be a reasonable "baseline" under the melting peak and measure the peak area above this baseline. The baseline estimation, however, is a highly subjective operation. For very sharp melting peaks, such as obtained with pure organic compounds, errors in baseline estimation are usually negligible. However, polymer melting peaks often extend over as much as 100°C; it is extremely difficult to determine precisely where the melting begins; and instrumental baseline curvature may be significant in the region of interest. Consequently, the answer obtained in polymer heat of fusion measurements is strongly dependent on the analyst's estimate of the extent and shape of the baseline to be drawn under the peak.

Another somewhat more subtle problem which contributes to the uncertainty is the fact that the DSC "instrumental baseline" on either side of the melting peak is not a "no-signal" line. Even in the absence of a transition, the instrument is measuring the heat capacity of the sample; and this varies as a function of temperature.

Even though this variation is nearly linear, over a wide temperature range curvature can be quite noticeable. Moreover, the heat capacity of amorphous or melted polymer is usually quite different from that of crystalline polymer. When we take these facts into account, the thermal behavior of a polymer in the melting region becomes quite complex. Prior to the melting the instrument records the heat capacity of the sample which is itself a function of the initial crystallinity and of temperature. When melting begins we will be recording the sum of the energy associated with the instantaneous rate of fusion plus the heat capacity of the instantaneous crystalline content and the heat capacity of the instantaneous amorphous content. After melting we record the heat capacity of the completely molten or amorphous polymer which, of course, should be independent of the original crystallinity but is still a function of temperature.

Our problem is to extract from this complicated sum of thermal effects that part of the energy which can be assigned directly to the melting of crystallites. The same problem arises in the analysis of data obtained by conventional calorimetry — it is in the nature of polymer melting behavior and not a peculiarity of the DSC or DTA method. Dole[9] has shown very clearly how the thermal behavior of a melting polymer can be described mathematically and how calorimetric data obtained by adiabatic calorimetry should be analyzed for the purpose of measuring the crystallinity. The same treatment can be applied to the analysis of DSC or quantitative DTA data, and it is the object of this paper to develop and examine several different methods of melting peak analysis which have theoretical justification and which therefore remove the subjectivity and hence uncertainty in polymer crystallinity measurements.

THEORY

As in all methods of crystallinity determination based upon the two-phase model, certain assumptions are made in the data analysis. These assumptions are often questioned, but it is outside the scope of this paper to discuss them in detail. Reference should be made to Dole's review articles for a critical evaluation and a bibliography of publications dealing with the assumptions and applicability of the calorimetric method. Here, it is sufficient to list the premises for the following treatment. It is assumed,

(*1*) that a semicrystalline polymer consists of, or at least behaves as if it consists of distinct crystalline and amorphous regions. Effects of size, perfection and surface properties of the crystalline regions are not considered;

(*2*) that the polymer is in an essentially stress-free state; that is, that stored energy effects due to orientation and the like are absent;

(*3*) that the crystalline regions at any particular temperature may be assigned a particular heat content, H_c, (calories per gram) and specific heat $\mathrm{d}H_c/\mathrm{d}T = C_c$ ($\mathrm{cal \cdot g^{-1} \cdot deg^{-1}}$);

(*4*) that the amorphous regions at any particular temperature may be assigned a particular heat content, H_a and specific heat $\mathrm{d}H_a/\mathrm{d}T = C_a$;

(*5*) that the amorphous regions are "liquid-like"; that is, that they have the same properties as the molten polymer and that therefore H_a and C_a at a particular temperature are identical to, or extrapolations from, the properties of the melt;

(*6*) that if x_T is the weight fraction of crystalline material at any temperature, T, then the heat content of the polymer and the total specific heat at temperature T are given by

$$H_T = x_T H_{cT} + (1-x_T) H_{aT} \tag{1}$$

$$\begin{aligned} C_T &= x_T \frac{\mathrm{d}H_{cT}}{\mathrm{d}T} + (1-x_T)\frac{\mathrm{d}H_{aT}}{\mathrm{d}T} \\ &= x_T C_{cT} + (1-x_T) C_{aT} \end{aligned} \tag{2}$$

By definition, the heat of fusion, $\Delta H^0{}_{FT}$, the energy required to transfer one gram of purely crystalline material to one gram of purely amorphous material at the temperature T is given by

$$\Delta H^0_{FT} = H_{aT} - H_{cT} \tag{3}$$

It should be noted that the above assumptions are precisely the same, with a simple transformation of notation, as those which are made in the application of specific volume or density measurements to the determination of crystallinity. Therefore, the theoretical basis for the calorimetric method is no more or less unsound than that for the widely used density method. In fact, these or analogous assumptions *must* be made for *any* "single point" method of crystallinity determination. A more complicated model would require more complicated methods or several measurements of different kinds.

Now going back to Eqn. (1), let us consider the total change in heat content; that is, the heat absorbed by the sample at constant pressure, as we change its temperature from some point, say room temperature to another temperature above the point where melting is completed.

At the initial temperature T_1 we have

$$H_1 = x_1 H_{c1} + (1-x_1) H_{a1} \tag{4}$$

At the final temperature T_2, $x = 0$ since we are above the final melting point. Therefore

$$H_2 = H_{a2} \tag{5}$$

By difference

$$\begin{aligned} \Delta H_{2,1} &= H_2 - H_1 = (H_{a2} - H_{a1}) + (H_{a1} - H_{c1}) x_1 \\ &= \Delta H_{a(2.1)} + \Delta H^0_{F1} x_1 \end{aligned}$$

Solving for x_1, the crystallinity at the initial temperature

$$x_1 = \frac{\Delta H_{2,1} - \Delta H_{a(2.1)}}{\Delta H^0_{F1}} \tag{6}$$

Thus the crystallinity of a polymer sample at T_1 can be determined by measuring the *total* energy absorbed by the sample per gram from T_1 to a temperature above the final melting point, T_2; subtracting the amount of energy which would be absorbed by one gram of a totally amorphous sample in the same temperature interval and dividing by the heat of fusion at T_1 of one gram of a perfectly crystalline sample. The calculation is most easily visualized from Fig. 1, a conventional *H vs. T* plot for a typical semicrystalline polymer.

Now, it is interesting to look at the meaning of Eqn. (6) as applied to data obtained with a differential scanning calorimeter which in effect records dH/dT. This is shown in Fig. 2. $\Delta H_{2,1}$ is the area ACDEF, $\Delta H_{a(2,1)}$ is the area ABEF and the difference is BCDG, which is the correct area to measure if we are going to refer our heat of fusion to the temperature T_1. Note that the correct baseline under the peak in this case is *the extrapolation of the recorded baseline from above the final melting point*. It should *not* be drawn tangent to the pre- and post-melting lines as is the common practice.

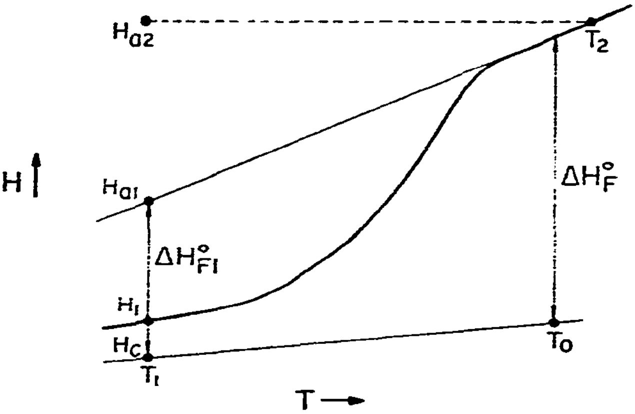

Fig. 1. Typical enthalpy plot in the melting region of a semicrystalline polymer.

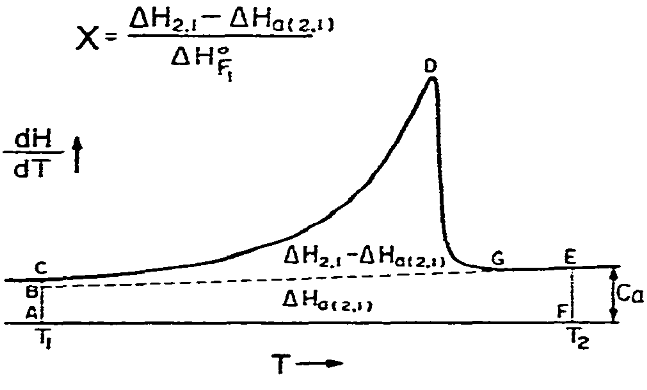

Fig. 2. Typical DSC polymer melting curve and instrumental baseline; the illustrated division of areas and calculation apply to crystallinity determination using the perfect crystal heat of fusion at T_1.

The division of areas as shown in Fig. 2 and the use of *Eqn.* (6) has a number of practical disadvantages. For example, it may not be possible to extrapolate the line EG a great distance with reasonable accuracy especially if EG is not linear, either because C_a is not a linear function of temperature or the instrumental baseline is curved. Also, we may not be able to record a sufficient length of EG for accurate extrapolation because of polymer decomposition at temperatures not very far above the final melting point.

Another problem is the determination of the value of ΔH^0_{F1}, the denominator of Eqn. (6). Since it is rarely possible to prepare polymers with 100% crystallinity, the "perfect crystal" heat of fusion usually has to be estimated or determined with the help of some other independent means or extrapolation technique. For example, the "perfect crystal" heat of fusion of polyethylene has been estimated by extrapolation from high molecular weight hydrocarbon values and also by plotting specific volume *vs.* heat of fusion for a number of samples and extrapolation to the perfect crystal specific volume as calculated from X-ray lattice parameters. More recently, nearly perfect crystals of polyethylene have been prepared by high pressure crystallization from the melt so that a direct measure could be made[12]. All of the various methods lead to a value of 69 ±1 $\text{cal}\cdot\text{g}^{-1}$ for polyethylene *at its perfect crystal melting point*. Relatively little work of this kind has been reported for other polymers and the fact that the perfect crystal heat of fusion is not well known is one of the disadvantages of the calorimetric method for crystallinity determinations. The problem is not fundamental, however — its resolution requires only that systematic calorimetric measurements combined with other techniques be carried out for other polymers as has been done for polyethylene.

Note that we have emphasized that even when the perfect crystal heat of fusion is known with confidence the value obtained usually refers to the temperature of the perfect crystal melting point, whereas in Eqn. (6) the value to be used is that at the initial temperature. Since the initial temperature is usually near room temperature, the difference between these two points can be a few hundred degrees. From the well-known equation for the variation of ΔH_F with temperature

$$\frac{\mathrm{d}\Delta H_F}{\mathrm{d}T} = \Delta C = C_a - C_c \tag{7}$$

we can see that a not unusual value of ΔC of as little as 0.1 $\text{cal}\cdot\text{g}^{-1}\cdot\text{deg}^{-1}$ leads to a change in ΔH_F of the order of 10 $\text{cal}\cdot\text{g}^{-1}$ for every one hundred degrees change in the reference temperature.

Given ΔH^0_F, the perfect crystal heat of fusion at the perfect crystal melting point, we need to calculate ΔH_{F1}; and for this we need to known C_a and C_c as a function of temperature. But here again, we require further careful calorimetric work to obtain these data — even in the case of polyethylene there is considerable disagreement among the various equations for C_a and C_c which have been reported[9].

However, we can obtain other equations relating x_1 to the measured enthalpy change by making use of the fact that $\Delta H_{2,1}$ should be independent of the path taken from T_1 to T_2. Thus we can imagine $\Delta H_{2,1}$ as being made up of three components for a particular path involving three stages. In the first we imagine that we heat from T_1 to T_0, the perfect crystal melting point while keeping x constant. Then,

$$\Delta H_{0,1} = x(H_{c0}-H_{c1})+(1-x)(H_{a0}-H_{a1}) \tag{8}$$

Now at T_0 we allow the crystals to melt

$$\Delta H_{F0} = x\Delta H_F^0 \tag{9}$$

Finally, we heat the molten polymer from T_0 to T_2

$$\Delta H_{2,0} = H_{a2}-H_{a0} \tag{10}$$

$\Delta H_{0,1}+\Delta H_{F0}+\Delta H_{2,0}$ must equal $\Delta H_{2,1}$

On a DSC record it is quite easy to draw the areas which correspond to each of these steps as shown in Fig. 3.

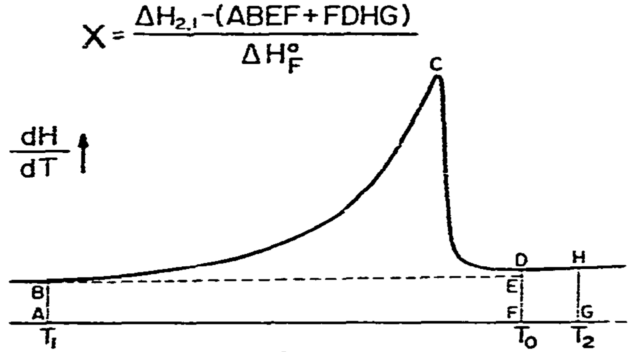

Fig. 3. DSC polymer melting curve and instrumental baseline; the division of areas and calculation apply to crystallinity determination using the perfect crystal heat of fusion at T_0, the perfect crystal melting point.

From Eqn. (8), $\Delta H_{0,1}$ is the area ABEF, the dashed line being the extrapolated line from the low temperature region where it is assumed no melting is taking place. From Eqn. (10), $\Delta H_{2,0}$ is the area DHGF. The rest of the area, BCDE, must therefore be ΔH_{F0} in Eqn. (9), and we obtain the crystallinity from Eqn. (9) by dividing ΔH_{F0} by ΔH_F^0.

Thus we conclude that if we wish to use the heat of fusion of the perfect crystal at the perfect crystal melting point, as the denominator, we must begin our DSC measurement at a temperature so low that we can record the baseline over a region where no melting takes place. We must then extrapolate this line up to T_0 and measure the total area above it to obtain ΔH_{F0}.

Here again we see that in general the proper baseline to draw will not be the one which we normally draw intuitively. In the case of polyethylene, however, there is a fortuitous circumstance. It happens to be found experimentally that the specific heat curves for pure crystalline and pure amorphous polyethylene cross in the neighborhood of 140°C which also is very close to T_0, the perfect crystal melting point[13]. From Eqn. (2) we see that at the temperature where C_{cT} happens to equal C_{aT} all semicrystalline specific heat curves independent of their crystallinity will cross the amorphous specific heat curve. Consequently, for polyethylene all extrapolated dashed lines should cut the "post-baseline" at the point D. Thus, the correct baseline for any polyethylene, assuming the absence of or correction for instrumental baseline curvature, is drawn by laying a ruler so that it pivots about the point D at 140°C and so that it is tangent to the curve at low temperature where no melting is assumed to take place.

For other types of polymers, more serious practical difficulties can interfere. For example, the low temperature part of the curve which we have to extrapolate may be confused by the presence of glass transitions or other discontinuities in the specific heat curve.

The above considerations show that the determination of the heat of fusion of a polymer from a DSC melting peak and the subsequent calculation of the crystallinity is a little more involved than is commonly assumed. The complexity arises from the facts that polymers melt over a very wide range of temperature so that the "rate-of-melting" or the amount of melting per degree is generally small and in energy units becomes comparable in magnitude to the specific heat of the polymer. Thus the effect of changing specific heat and the fact that the heat of fusion is a function of temperature have to be considered in the curve analysis.

We can see this from Eqn. (1), which gives H at any temperature.

$$H = xH_c + (1-x)H_a \tag{1}$$

remembering that x, H_c and H_a are functions of temperature and that $H_a - H_c = \Delta H_F$, we find by differentiation with respect to T

$$\frac{dH}{dT} = xC_c + (1-x)C_a - \Delta H_F \frac{dx}{dT}$$

$$\frac{dH}{dT} = C - \Delta H_F \frac{dx}{dT} \tag{11}$$

Since the quantity recorded as ordinate in DSC which is essentially dH/dT is made up of two terms, a heat capacity term which is a function of both temperature and x, and the fusion term which is a function of the rate of melting. Where dx/dT is small, as at the beginning of melting, the fusion term is small with respect to the specific heat. In fact, for many polymers, nylons, for example, the specific heat terms remain comparable or greater in magnitude than the fusion term throughout the entire melting. This is quite unlike the situation for sharply melting materials, such as pure metals or organic compounds where the instantaneous rate of melting (the DSC peak height) is so great and the peak so narrow that specific heat variations are virtually negligible with respect to the fusion.

Even though the proper analysis of a polymer melting curve is complex, it would be quite easy to determine a correct baseline method if we had reliable values for ΔH_F^0 and for C_a and C_c as a function of temperature. However, there have simply not been sufficient systematic calorimetric studies of polymers to produce reliable values — with a single possible exception in the case of polyethylenes. With the availability of fast scanning differential scanning calorimeters of more than adequate accuracy for the purpose, there is nothing to prevent the rapid accumulation of the required data.

A suggested approach to the development of an objective calorimetric method for crystallinity determinations goes back to Eqn. (6). Suppose we investigate a large number of samples of a particular polymer type and of varying crystallinity between the same two limits of temperature, T_1 and T_2. Note that we can write Eqn. (6) in the form

$$x_1 = a\Delta H_{2,1} - b \qquad (12)$$

where $a = 1/\Delta H_{F1}$ and $b = \Delta H_{a(2,1)}/\Delta H_{F1}$ and are constants for this particular polymer type and the particular choice of T_1 and T_2. Thus Eqn. (12) says that the crystallinity and the *total* energy absorbed between T_1 and T_2 are linearly related. The total energy would be area ACDEF in Fig. 2 and would be measured most accurately by using the same experimental procedure for locating the "no sample" baseline which is used in specific heat determinations by DSC[14]. To determine the constants a and b, we need to have some independent means of measuring the crystallinity of at least two of the samples. For those polymers which can be obtained in the totally amorphous condition, an amorphous sample ($x_1 = 0$) provides one reference; and we need only know the crystallinity for one other. The independent means, of course, can be any that is felt to be the most reliable for the particular polymer type; specific volume, IR, X-ray, *etc.*

The above represents the minimum labor necessary to establish a practical objective method for crystallinity determinations by DSC. Of course, we can develop more information with respect to the values of the specific heats and heats of fusion from Eqn. (11) by more detailed studies; but since our object here is to suggest a method of analyzing a DSC curve for measurements of crystallinity which is free of problems associated with baseline extrapolations and interpolations, further applications will not be discussed.

There is one last but very important point to be made with respect to the measurement of crystallinity by DSC which relates to the fact that almost all practical polymer samples to some degree undergo either crystallization or melting followed by recrystallization while they are being heated through the melting region, even at relatively fast speeds[15]. An extreme case is that of an amorphous sample of polyethylene terephthalate which crystallizes on heating in the neighborhood of 150 and finally melts near 250°C. This sort of behavior seriously complicates baseline methods but has no influence at all on the suggested "total ΔH" approach. The total enthalpy change, $\Delta H_{2,1}$, should be a function of the initial and final states only; and since the final state is the polymer melt, the properties of which we assume are independent of previous history, $\Delta H_{2,1}$ should yield the correct crystallinity at the starting temperature regardless of the path which the polymer chooses to take. For example, the effect of crystallization during the run in the case of the amorphous polyester would be exactly compensated by opposite effects when the crystals melt.

Finally, it should be noted that a method of correcting the baseline for specific heat effects similar to those encountered in polymer melting curves has been given by Brennan, Miller and Whitwell[16]. An analogous method could be adopted, but it involves considerable subjectivity and potential error in extrapolating pre- and post-melting baselines over the long distances found necessary for many polymer fusion curves. At least for this application, we believe that the "total ΔH" approach is less subject to operator bias.

EXPERIMENTAL

To measure the total energy absorbed by a sample between two temperatures T_1 and T_2 using the Perkin–Elmer Model DSC-1B differential scanning calorimeter, two scans must be made over the range. The first scan is made under the selected conditions with an empty sample pan and cover. The instrument is allowed to come to thermal equilibrium at the temperature T_1 — this condition is met when the pen draws a horizontal "isothermal line" on the chart. The scan is then started. The pen will displace either in the positive or negative direction and draw a "no-sample baseline". The amount and direction of shift from the isothermal line will depend upon the net difference in heat capacity between the sample and reference sides, the setting of the "slope control", *etc*., but is immaterial to the experiment so long as the pen remains on scale over the range of interest. When the temperature reaches T_2, the scan is stopped; and the pen is again allowed to come to isothermal equilibrium

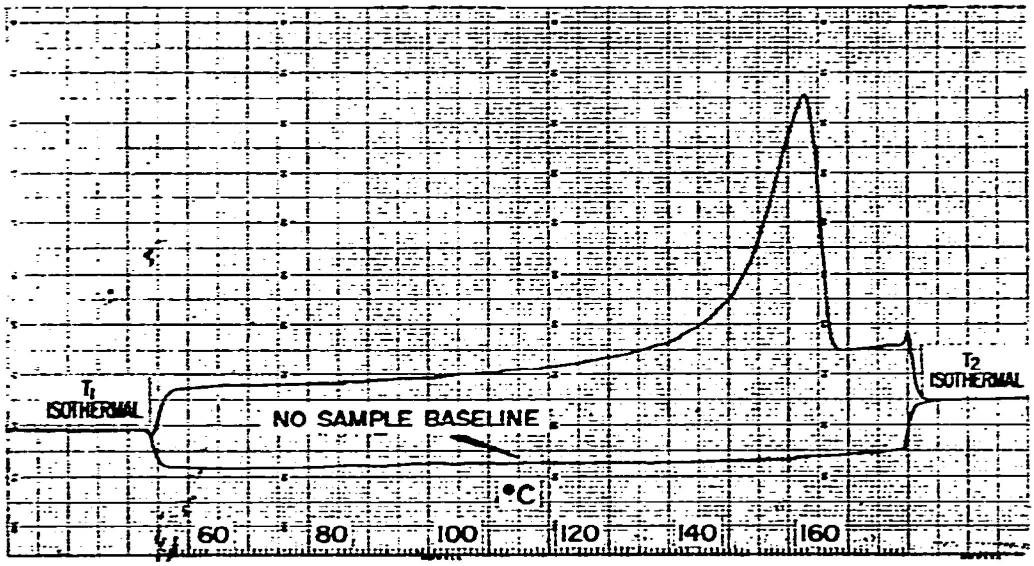

Fig. 4. DSC polypropylene melting curve and "no sample" baseline.

drawing a horizontal isothermal line at T_2. Such a "no-sample" baseline is illustrated in Fig. 4.

Using the same sample pan and cover or ones of equal total weight, the sample is then encapsulated and placed in the instrument which has been cooled to T_1. Again the scan is made from equilibrium at T_1 to equilibrium at T_2. In this sort of experiment, just as in specific heat determinations[14], it is essential that the conditions of the second scan be the same as the first since the difference between the two is to be interpreted as solely due to sample energy absorption. The position of the T_1 and T_2 isothermal lines on the chart provide a check on the reproducibility of the conditions and therefore the validity of the experiment. At isothermal equilibrium the instrument cannot detect the presence of the sample because under these conditions the differential power system has only to correct for differential heat losses from the holders to the surroundings; and these should be unaffected by the presence of a sample in the covered pan — the differential heat capacity is only detectable when we change the temperature; that is, start the scan. Accordingly, if the T_1 and T_2 "isothermals" of the second scan are identical in position on the chart to those in the first scan, we can be confident that all conditions have been duplicated and that the difference between the two scans is a valid measure of $\Delta H_{2,1}$.

The optimum choice of operating conditions in such a measurement is determined by the following factors. Remembering that we are interested only in a total area measurement, not in resolution or peak temperature accuracy,

(*1*) the temperature calibration need be accurate only at T_1 and T_2 — it doesn't matter if the calibration is nonlinear in between;

(*2*) the sample size is relatively immaterial — it is advisable to use reasonably large samples and low instrument sensitivity to enhance the baseline reproducibility. Thermal gradients in the sample which would be serious if resolution or dynamic temperature accuracy were of interest have no effect in the total ΔH measurement, which depends only on the initial and final isothermal states;

(*3*) the choice of scanning rate is not critical. Again, it is only the initial and final states which influence $\Delta H_{2,1}$. It is advisable to use reasonably fast rates of 10 or 20°C/min to increase the effective ordinate sensitivity and also reasonably fast chart speeds to increase abscissa sensitivity, yielding a large total area. It is better to increase sensitivity in this way than by increasing instrumental sensitivity since the latter change will magnify changes in both the isothermals and the scanning portions, whereas an increase in scanning rate magnifies the change in the scanning portions only.

In short, the conditions of instrument sensitivity, sample size, and scanning rate are chosen to give a large displacement of the sample run relative to the no-sample run but at the same time to make the isothermals easy to reproduce. The domed aluminum holder covers or radiation shields which are provided with the instrument and with the "specific heat kit" for the purpose of enhancing baseline reproducibility are used at all times.

To measure the area which corresponds to $\Delta H_{2,1}$, it is convenient to superimpose the two scans on a "light box" and trace the "no-sample" run on the sample run. Within limits, mismatch of the isothermals can be compensated by slight relative tilting so that the isothermals match perfectly. Fig. 4, a scan of a sample of polypropylene between 50 and 175°C, is a typical example. The total area between the two runs may be integrated with a planimeter and converted to calories through the use of the instrumental area-to-calories conversion constant. However, in our laboratory this sort of measurement is of such general utility that we have developed a computer program which performs the following operations:

(*1*) subtracts the no-sample baseline from the sample run, thus correcting for instrumental baseline curvature and referencing all ordinate displacements to the isothermal lines;

(*2*) interpolates a straight line between the isothermals at T_1 and the isothermal at T_2 extrapolated back to T_2, where the scan was stopped;

(*3*) performs cumulative and total area integration;

(*4*) converts all temperatures to true sample temperatures by correcting for thermal lag;

(*5*) prints out, at the operator's option, cumulative area in cal·g^{-1} *vs.* sample temperature or ordinate displacement in specific heat units (cal·g^{-1}·deg^{-1}) *vs.* sample temperature;

(*6*) with a digital plotter (Houston Instruments "Complot" or equivalent), the same data as in (*5*) can be scaled and plotted with appropriate axes.

An example of the computer plot for the same data of Fig. 4 is shown in Fig. 5. Both cumulative area in units of ΔH and the corrected re-plot of the digital data in units of $\mathrm{d}H/\mathrm{d}T$ are conviently drawn on the same record.

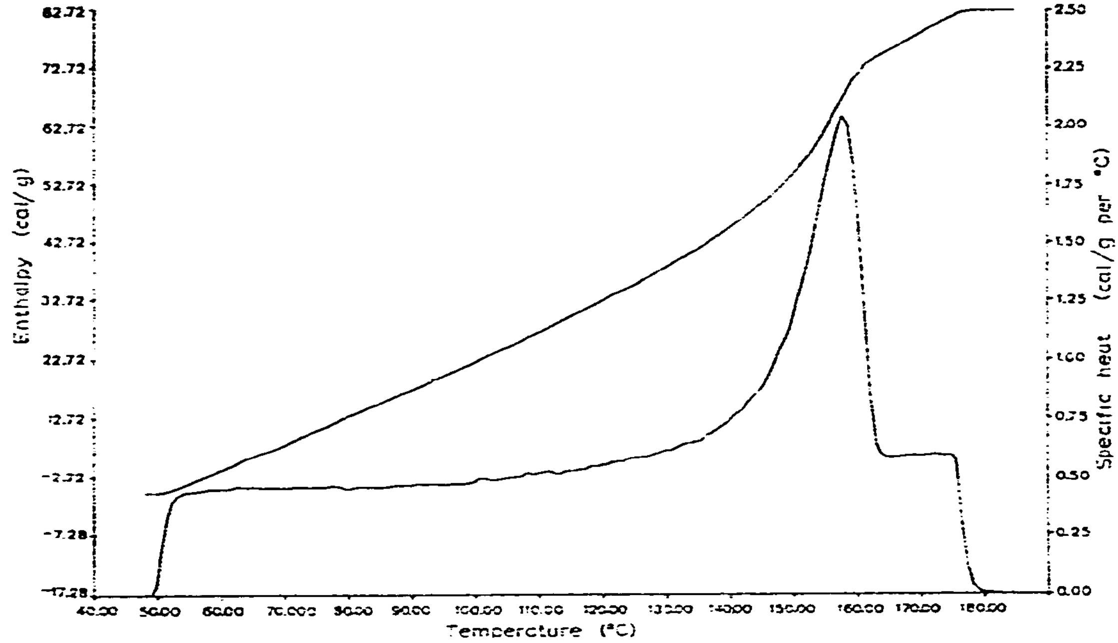

Fig. 5. Computer plot of reduced DSC data from scans of Fig. 4.

The data were obtained in digital form on punched paper tape through the use of the Perkin–Elmer ADS VI digital data system for thermal analysis[17] and were analyzed off-line using the Perkin–Elmer Scientific Computer Facility time-sharing system.

RESULTS AND DISCUSSION

The polypropylene data of Fig. 5 illustrate most of the points made in the introductory section. The broad melting range is evident; and assuming reasonable linearity of the specific heat functions, it appears that melting begins at least as low as 105°C. Both the specific heat and the enthalpy plot show that the energy in the fusion peak is a relatively small proportion of the total energy in the range of melting. Note that the effective "specific heat" at the peak maximum is only of the order of 2.00 $\mathrm{cal \cdot g^{-1} \cdot deg^{-1}}$. This is to be contrasted with Fig. 6, a comparable plot of an indium melting peak. Here the effective "specific heat" at the peak maximum is nearly 12.00 $\mathrm{cal \cdot g^{-1} \cdot deg^{-1}}$. Consequently, in the region of melting for indium, the *actual* specific heat of indium is negligible with respect to the melting peak — such a heat of fusion can be measured with high accuracy without correcting for specific heat effects at all; and there is no question about where the baseline should be drawn.

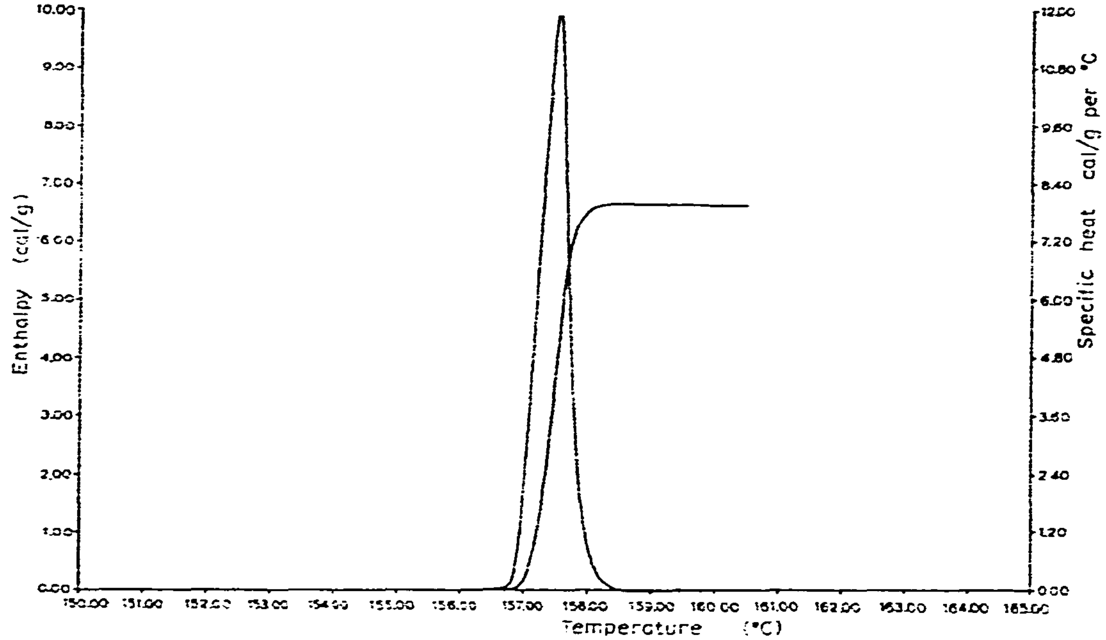

Fig. 6. Computer plot of indium melt.

To comment further on the polypropylene plot of Fig. 5, it appears that up to about 90°C no significant melting is taking place and that a good estimate of the heat of fusion could be made by drawing a tangential line between say 100 and 170°C. In this particular case, this may well be true; but such an assumption is hazardous. The appearance of a reasonably linear portion of the data at lower temperatures may well be due to a combination of effects — the signal is always the sum of specific heat, endothermic melting, and exothermic crystallization. In poorly crystallized samples, the latter may seriously depress the baseline below the actual specific heat level; and the tangentially drawn baseline would be correspondingly in error.

Only after a very large number of samples of widely varying average molecular weight, degree of tacticity, *etc.*, and particularly of different thermal histories have been examined in detail in a manner such as illustrated in Fig. 5, can we be confident of the true nature of the melting behavior of any particular polymer type.

As further examples, Figs. 7 and 8 are computer plots of similar data obtained on samples of high density and low density polyethylene, respectively. The scales in the two figures are the same to emphasize the substantial differences in melting "intensity" which can be observed within the same polymer class. Obviously the area of the high density melting peak could be measured with a baseline technique with small error. On the other hand, it is not at all apparent where such a baseline should be drawn in the case of the low density sample. The "total ΔH" method is free of such ambiguities. As was pointed out in the introduction, a few reliable correlations with other methods of crystallinity determination are sufficient to establish the relationship between x and $\Delta H_{2,1}$, once and for all. The data obtained on the samples of Figs. 7 and 8 are discussed in more detail elsewhere[18].

In some cases, the "total ΔH" method of crystallinity measurement is a necessity. Many polymer classes are well known for their tendency to crystallize on heating, especially if their previous thermal history involved rapid cooling from the melt. The most frequently studied example is polyethylene terephthalate. Fig. 9 shows three superimposed computer plots of the same sample of polyethylene terephthalate heated from 50 to 275°C after being subjected to three different thermal histories. Obviously the area of the melting peak at 250°C provides no information on the initial crystallinity. A procedure that is sometimes used is to measure the melting peak area and from this substract the exothermic crystallization peak area to obtain a measure of the initial crystallinity. This measure, however, will be quite inexact if only because the heat of fusion and therefore the heat of crystallization per unit crystallinity will be quite different near 150 from that at 250°C (see Eqn. 7) — unless ΔC is fortuitously zero over this range. Moreover, it can be seen from Fig. 9 that differences in initial crystallinity are manifested over the entire range of the thermograms — note particularly the substantial differences in effective "specific heat" over the range from 160 to 220°C. These differences have almost as much effect on the measurement as the existence of the crystallization peaks even though they are not at all evident on casual inspection of the individual thermograms.

The cumulative enthalpy plots terminate in values of $\Delta H_{2,1}$, equal to 96.8 for the liquid nitrogen shock-cooled sample, 101.9 for the room temperature shock-cooled sample, and 107.5 for the sample cooled from the melt at 10°C/min. The sample cooled from the melt in liquid nitrogen can be assumed to be completely amorphous

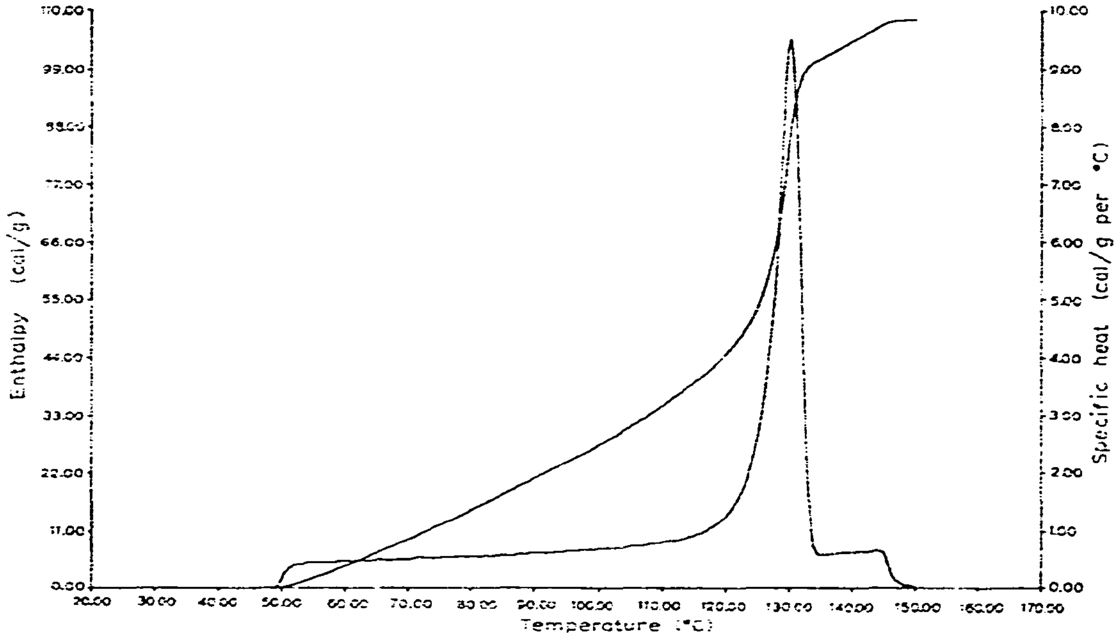

Fig. 7. Computer plot of reduced DSC data for a 3.490 mg sample of linear polyethylene.

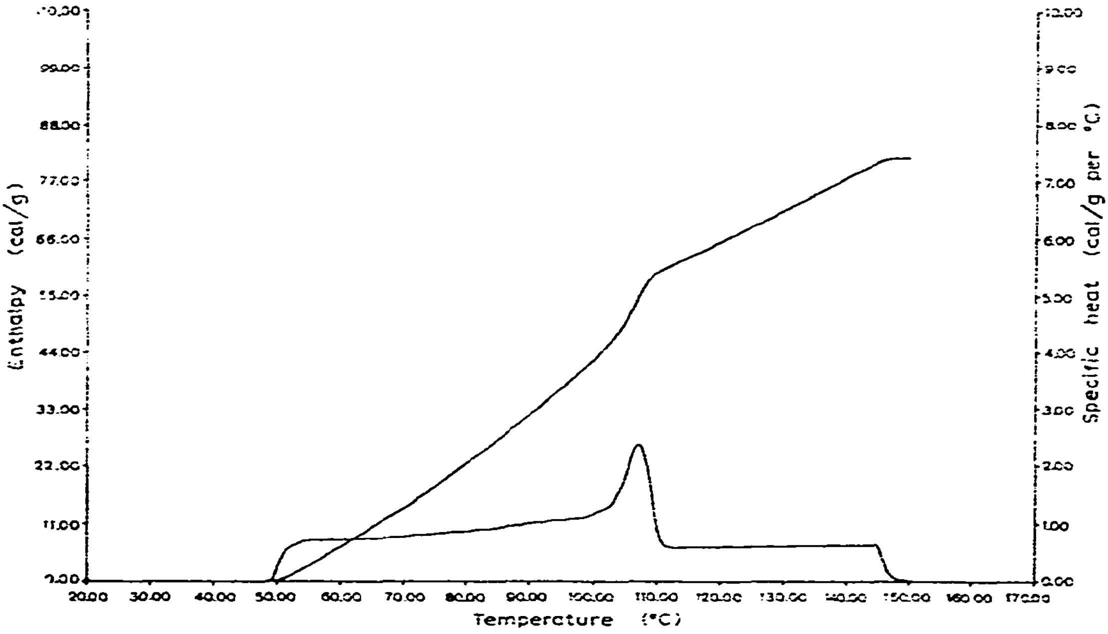

Fig. 8. Computer plot of reduced DSC data for a 10.64 mg sample of low density polyethylene.

at T_1; so that as pointed out in the introduction, we have a direct measure of $\Delta H_{a(2,1)}$; and we require only one independent measure of a semicrystalline sample to determine the constants of Eqn. (12) for polyethylene terephthalate. Even without this additional measurement, the *relative* crystallinity of a series of PET samples can be

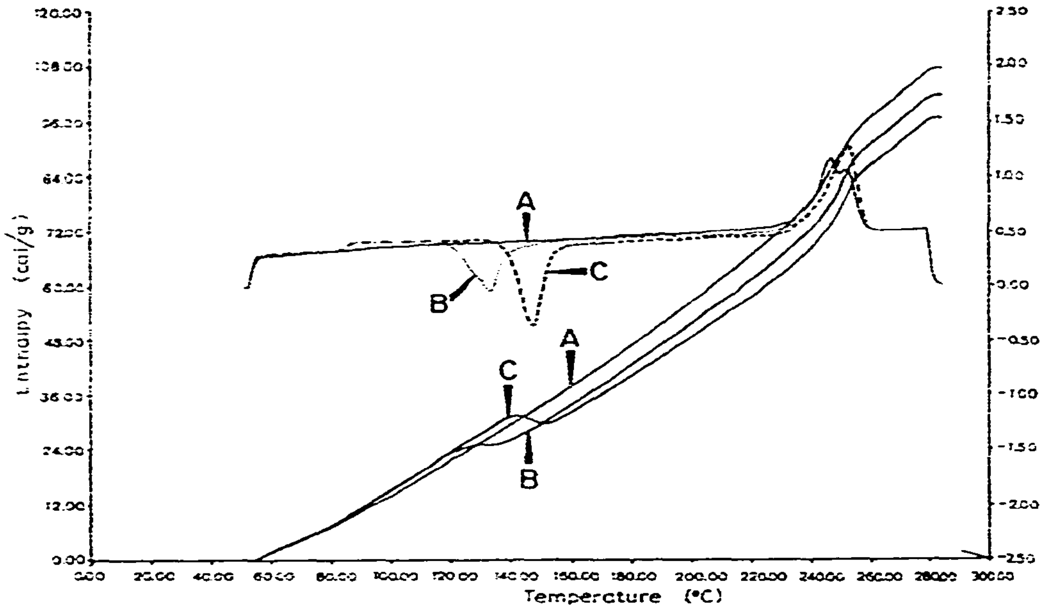

Fig. 9. Superimposed computer plots of the melting of a sample of polyethylene terephthalate after three different thermal histories; (A) crystallized from the melt at a cooling rate of 10°/min; (B) shock-cooled from the melt to room temperature; (C) shock-cooled from the melt in liquid nitrogen.

measured reliably using the data already obtained. For example, the crystallinities of the above sample in the two semicrystalline cases are in the ratio (107.5 − 96.8)/(101.9 − 96.8).

SUMARY AND CONCLUSIONS

It has been shown that in the absence of an extensive body of literature dealing with calorimetric measurements of polymers of all types, traditional "baseline" methods of measuring polymer heats of fusion by DSC and quantitative DTA involve highly subjective decisions which lead to errors, lack of interlaboratory agreement, and uncertainties in the comparison of calorimetric results with other methods for crystallinity determination. A procedure has been suggested which has the primary virtue of being clearly defined operationally but which also has universal applicability, even to samples which crystallize, or melt and recrystallize, on heating. The procedure involves little additional experimental effort over baseline methods and can quickly lead to a consistent, well-founded relationship between polymer crystallinity and enthalpy measurements by DSC. With the help of computer analyses, reliable calorimetric data can be generated at an unprecedented rate so that a series of experimental programs for the various polymer types can quickly resolve many of the problems and determine many of the unknown quantities which currently limit the applicability and reliability of scanning calorimetry in polymer crystallinity measurements.

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