

The measurement of the crystallinity of polymers by DSC

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Abstract

The procedures adopted and the inherent assumptions made in the measurement of crystallinity of polymers by differential scanning calorimetry (DSC) are reviewed. The inherent problem in all DSC measurements is concurrent recrystallisation and melting of the polymer sample on heating to the melting point and the variation of the enthalpies of crystallisation and melting, heat capacities and degree of crystallinity with temperature. A First Law procedure is suggested which involves heating the sample between two set temperatures, T_1 and T_2 . T_1 is selected by the requirement that the degree of crystallinity of the sample should not change either with temperature or time, and be representative of the sample during its use. T_1 is taken to be ambient or just above the glass transition temperature. T_2 is taken to be just above the observed last trace of crystallinity. Integrating the observed specific heat difference between the sample and the completely amorphous material during these two temperature ranges determined the residual enthalpy of fusion at T_1 . Problems are noted in the use of this procedure in that the specific heat of the liquid should not be arbitrarily chosen since this leads to systematic errors in the heat of crystallisation.

The degrees of crystallinity of metallocene polyethylene (m-PE) and polyethylene terephthalate (PET) measured by this procedure have been compared with values measured by density, determined at room temperature. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The degree of crystallinity is the single most important characteristic of a polymer in that it determines mechanical properties, such as yield stress, elastic modulus and impact resistance [1,2]. In particular, amorphous polyethylene terephthalate (PET) is of little commercial value since it has poor mechanical properties, low dimensional stability and high gas permeation rate; on the other hand, crystalline PET has higher strength, good dimensional stability and chemical resistance. It is widely used in the production of fibres and in carbonated beverage containers because of its strength and low gas permeability, especially to carbon dioxide and oxygen.

The degree of crystallinity of a polymer is temperature-dependent [3] and in comparing its effect on material properties it is vital to carry out these measurements at the same temperature, invariably at ambient temperature and not at the melting point.

The various analytical methods used to determine the crystallinity of a polymer namely, wide angle X-ray diffraction (WAXD), density, differential scanning calorimetry

(DSC), infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy have been reviewed by Runt [4]. He considered that DSC was ‘probably the most widely used technique’. However, despite this, it is probably the most widely misused method [5–11]. The usual procedure in measuring the degree of crystallinity by DSC involves drawing a linear arbitrary baseline from the first onset of melting to the last trace of crystallinity and determines the enthalpy of fusion from the area under this endotherm. The degree of crystallinity is then defined as

$$X_c = \Delta H_f(T_m) / \Delta H_f^0(T_m^0) \quad (1)$$

where X_c is the weight fraction extent of crystallinity, $\Delta H_f(T_m)$ is the enthalpy of fusion measured at the melting point, T_m , and $\Delta H_f^0(T_m^0)$ is the enthalpy of fusion of the totally crystalline polymer measured at the equilibrium melting point, T_m^0 . No correction is usually made for the variation in the specific heats with temperature or the differences between the liquid and crystalline values.

Some allowances have also been made for the sample crystallising on heating by separately integrating the exotherm on cold crystallisation and endotherm on melting over appropriate but different temperature regions. The degree of crystallinity is then defined as [8,11]

$$X_c = (\Delta H_f - \Delta H_c) / \Delta H_f^0 \quad (2)$$

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where ΔH_f is the enthalpy of fusion, ΔH_c the enthalpy of crystallisation and ΔH_f^0 the heat of fusion of the completely crystalline materials at the equilibrium melting temperature, T_m^0 . All are measured at different temperatures and no corrections are made for the change in specific heat. Nevertheless this method has appeared as a recommended method [12]. Both these methods define the degree of crystallinity close to the melting point rather than at room temperature where other analytical measurements are used, and there is little agreement between them. There are several things incorrect with both procedures. The integration baseline, separating exotherms and endotherms, is drawn arbitrarily and does not reflect the specific heats of the partially crystalline material or the liquid and has no physical meaning [13]. Secondly, the range between the end of crystallisation and the beginning of melting is not considered. It is assumed that no melting or recrystallisation occurs on heating. Because of these effects, the degree of crystallinity as measured by DSC conflicted with the values obtained by other methods [14,15]. Conventionally, specific heat differences and the temperature dependencies of the thermodynamic parameters are not considered [16,17]. Finally the enthalpy of fusion of 100% crystalline materials is invariably taken as the value at the equilibrium melting point, T_m^0 , rather than in the temperature region of the measurement [3,18,19].

In measuring the degree of crystallinity of Nylon-6, Khanna et al. [20] recommended a method, in which the baseline was drawn between two set temperatures, i.e. one post- T_g and the other above T_m . Although as the authors admitted, the samples post- T_g were a mixture of liquid and solid and the observed specific heat was dependent on the degree of crystallinity. It cannot be taken to represent the specific heat of the liquid line. Despite this a linear baseline between the two observed specific heats was drawn between these set temperatures. This separated the exotherm and endotherm due to recrystallisation and melting and determined the degree of crystallinity from Eq. (2) but overestimates the degree of crystallinity.

Some times ago, Gray [21] and Richardson [13] separately proposed a correct procedure to measure the crystallinity, in which the enthalpy of fusion was measured at the onset of the melting point by subtracting the enthalpy change for the super-cooled liquid from the total enthalpy change over all melting temperature ranges and then the crystallinity was measured at this temperature, i.e.

$$X_c = \Delta H_f(T_{\text{onset}}) / \Delta H_f^0(T_{\text{onset}}). \quad (3)$$

Later this method was called the total enthalpy method [19], however, it has appeared to be ignored by most polymer scientists. Recently, Mathot et al. [22–24] recommended the enthalpy-based crystallinity by using the following relationship, i.e.

$$X_c = \frac{h_a(T_1) - h_x(T_1)}{h_a(T_1) - h_c(T_1)}, \quad (4)$$

where $h_a(T_1)$, $h_c(T_1)$ and $h_x(T_1)$ are the enthalpies of the

completely amorphous, crystalline and semicrystalline sample at the temperature T_1 , respectively. Obviously, $[h_a(T_1) - h_x(T_1)]$ is the heat of fusion of semicrystalline sample at T_1 and $[h_a(T_1) - h_c(T_1)]$ is the heat of fusion of the 100% crystalline at T_1 . Mathot et al. [24] found that the crystallinity measured by this enthalpy procedure was in good agreement with the density procedure although it not necessary the same.

Recently Hay et al. [16,17] also proposed the First Law method. This evaluated the residual enthalpy of the sample at the lower temperature, T_1 , which should be room temperature or above but close to the glass transition, and determined the initial degree of crystallinity of the sample prior to heating. The residual enthalpy, ΔH_R , is the algebraic sum of the enthalpies of crystallisation and melting together with the specific heat changes with temperature for the partially crystalline solid, and for the liquid on cooling, as outlined in Fig. 2. This measured the crystallinity of the sample at T_1 closely reflecting the value at room temperature since the crystallinity did not change on heating to the glass transition.

Essentially, the last three methods are equivalent since the enthalpy of fusion is measured at the lower temperature and correction is made for the specific heat changes. In this paper, the degrees of crystallinities of m-PE and PET have been measured using the First Law method and the effect of specific heat baseline corrections evaluated.

2. Experimental

PET was supplied by DuPont Ltd as moulding pellets. It has a number average molecular weight of 19.6 kg mol^{-1} and weight average of 36.4 kg mol^{-1} . The m-PE was purchased from Exxon Chemical Co. France, as the Exact grade 3009. It is a copolymer of ethylene and hexene-1. The number and weight average molecular weights are 40 and 100 kg mol^{-1} , respectively.

PET was dried in a vacuum oven at 100°C for 12 h and pressed at 280°C for 2 min at a pressure of 7.5 MN m^{-2} into $100 \text{ mm} \times 100 \text{ mm} \times 0.8 \text{ mm}$ plaques. The plaques were quenched in ice water to obtain amorphous sheets. The m-PE was moulded at 160°C for 5 min under the same pressure. The plaques were then either quenched directly in water or slow-cooled in the hydraulic press to room temperature for 5 h. Discs were cut directly from the plaques for DSC analyses.

A Perkin–Elmer differential scanning calorimetry, DSC-2, interfaced to a PC was used to measure the thermal properties of the moulded samples. The calorimetry operated with a nitrogen flow $20 \text{ cm}^3 \text{ min}^{-1}$. The temperature of the calorimeter was calibrated from the observed melting points of distilled water and ultra-pure materials—stearic acid, indium, tin and lead—at heating rate of 10, 5 and 2.5 K min^{-1} . Thermal lag corrections were made by extrapolating to zero heating rate. DSC was used adopting the

procedure for measuring heat capacities. Empty aluminium pans, matched in weight to within 0.02 mg, were used for the sample and reference. Initially, the two empty pans were scanned to determine the calorimeter baseline and this was repeated with a sapphire standard sample to calibrate the thermal response of the calorimeter. Finally this was repeated with the polymer disc sample. The same heating rate of 10 K min^{-1} and sample weight of $10.00 \pm 0.03 \text{ mg}$ was used to obtain comparable results.

Densities were measured on moulded specimens by Archimedes' method: first by weighing in air and then in *n*-heptane at 296 K. An average of at least three determinations on separate specimens, taken from the same sample, were used.

3. DSC analysis

The First Law method is an application of the First Law of Thermodynamics to the crystallisation and melting of a polymer sample on heating in a calorimeter. It involves two separate measurements. The first one determines the overall enthalpy changes on heating a partially crystalline polymer from T_1 to above the melting point, T_2 . The second is a virtual experiment of measuring the enthalpy change on cooling the liquid from T_2 to T_1 without crystallisation occurring, see Fig. 1. For a closed system, the difference between these two steps is the enthalpy of fusion of the sample at T_1 , i.e.

$$\Delta H_R = \Delta H_{12} + \Delta H_{21} \quad (5)$$

in which

$$\Delta H_{21} = \int_{T_2}^{T_1} C_{p,a} dT \quad (6)$$

where ΔH_R is the residual enthalpy of fusion at T_1 , ΔH_{12} and ΔH_{21} are the changes in enthalpy on heating and cooling, respectively. $C_{p,a}$ is the specific heat of the amorphous material. ΔH_{12} includes the enthalpy changes due to the

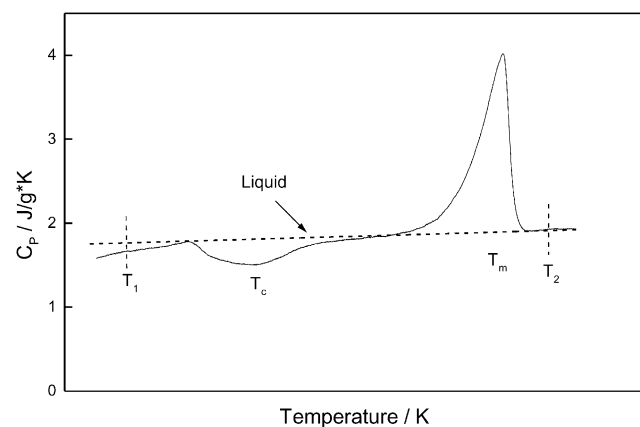


Fig. 1. DSC analysis of a partially crystalline polymer sample showing the presence of recrystallisation and melting.

change in specific heat of the partially crystalline sample between T_1 and T_2 , i.e. $\int C_{p,x} dT$, allowing for it to change with degree of crystallinity, crystallisation, annealing and recrystallisation, ΔH_c , as well as partial melting at intermediate temperatures, and final melting ΔH_f . For an initially amorphous sample ΔH_R should be zero. The DSC analysis for partially crystalline sample and the enthalpy changes in these processes are shown diagrammatically in Figs. 1 and 2, respectively.

The amorphous liquid temperature dependence, $C_{p,a}$, can be obtained by several methods, i.e. by a linear extrapolation of the specific heat of the liquid measured in the melt; or measured on an amorphous sample above the glass transition temperature prior to the onset of crystallisation or by using reference data. In the first two cases, heat flow measurements in the calorimeter can be used directly instead of the measured specific heat.

The weight fraction degree of crystallinity at T_1 , $X_c(T_1)$, is then the ratio of the observed enthalpy of fusion of the sample to that of the completely crystalline material at T_1 ,

$$X_c(T_1) = \Delta H_f(T_1)/\Delta H_f^0(T_1) = \Delta H_R/\Delta H_f^0(T_1). \quad (7)$$

Normally, the ΔH_f^0 is measured at equilibrium melting point T_m^0 , and not at T_1 ; however,

$$d(\Delta H_f^0) = (C_{p,a} - C_{p,c})dT = \Delta C_{p,c} dT \quad (8)$$

where $\Delta C_{p,c}$ is the specific heat difference between the completely liquid and crystalline solid, $C_{p,c}$. The enthalpy of fusion of 100% crystalline value at T_1 could be obtained by integrating the above equation from T_1 to T_m^0 ,

$$\Delta H_f^0(T_1) = \Delta H_f^0(T_m^0) - \int_{T_1}^{T_m^0} \Delta C_{p,c} dT. \quad (9)$$

Once $\Delta H_f^0(T_1)$ is obtained, the crystallinity is readily calculated from Eq. (7).

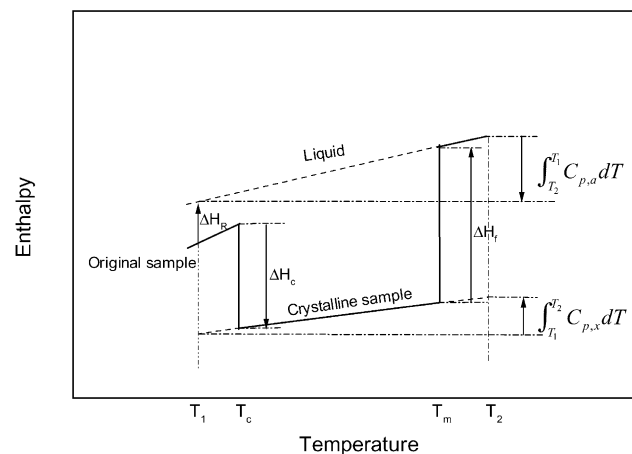


Fig. 2. Schematic of the enthalpy changes on recrystallisation and melting between two set temperatures, T_1 and T_2 .

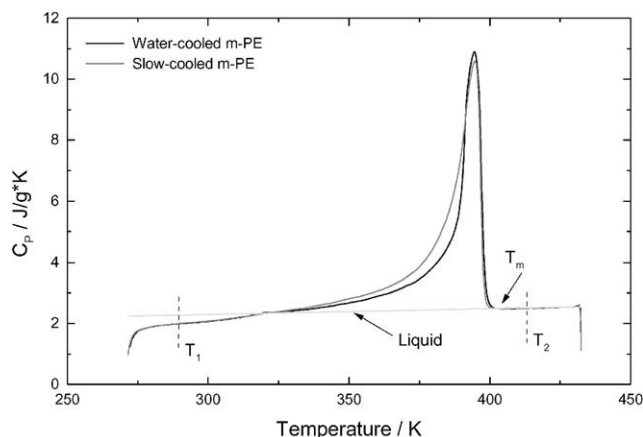


Fig. 3. DSC analyses of m-polyethylene samples along with the amorphous specific heat temperature dependence, extrapolated from the molten state.

4. Results and discussion

4.1. The fractional crystallinity of m-PE

Fig. 3 shows the DSC analyses of water and slow-cooled m-PE samples. m-PE has good thermal stability above T_m and the amorphous specific heat–temperature dependence is well-defined. It is drawn directly onto the DSC thermal response above the melting point and extrapolated to ambient temperature [19,24].

The heat of fusion at 298 K was determined using the First Law method as 116 and 132 J g⁻¹ for the water and slow-cooled samples, respectively. The heat of fusion of completely crystalline PE at 298 K was determined [25] to be 243.8 J g⁻¹, which is approximately 17% less than the more commonly used value of 293 J g⁻¹ at the equilibrium melting point. The fractional crystallinities of the water and

slow-cooled sample were 0.48 ± 0.02 and 0.54 ± 0.02 , respectively. These values compared well with the weight fraction crystallinity measured by density at 296 K. They are listed in Table 1. Mathot [24] found that the melting of very low-density polyethylenes could occur as low as -60 °C and the crystallinities were as much as 40% higher than that at room temperature. In such situation, the degree of crystallinity must be measured at the same temperature, otherwise no comparison can be made with the values determined by other means.

4.2. The fractional crystallinity of PET

PET, amorphous to WAXD and by density measurements, was observed by DSC to have a glass transition at about 353 K, see Fig. 4a and a large exothermic crystallisation at about 410 K. Melting finally occurred above 500 K, although modulated temperature DSC studies indicated that considerable melting and annealing occurred prior to final melting [28]. There were two temperature regions in which only liquid existed—one post- T_g and prior to the onset of crystallisation and the other above T_m . Careful measurement of the heat capacities in these temperature regions indicated that they exhibited different temperature dependencies and the PET was degrading above T_m . As a result, the post- T_g amorphous specific heat–temperature dependence was chosen. The residual enthalpy of fusion determined just above the T_g for these amorphous samples was zero. The determinations were repeated 10 times and the variation in fractional crystallinity was ± 0.02 , as shown in Table 2. The results are highly reproducible and consistent with WAXD and density results.

Fig. 4b displays the DSC analyses of PET samples crystallised in a vacuum oven at 383 K for different period times. They exhibited less well-defined glass transitions and

Table 1
Fractional crystallinities measured by density and residual enthalpies of fusion

Sample	Density (g cm ⁻³)	Residual enthalpy (J g ⁻¹)	Fractional crystallinity by	
			Density ± 0.02	DSC ± 0.02
m-PE				
Water-cooled m-PE	0.923	116	0.51	0.48
Slow-cooled m-PE	0.931	132	0.57	0.54
PET				
Amorphous	1.336	0.4	0.01	0.00
110 °C, ^a 1 h	1.350	9.6	0.09	0.10
110 °C, ^a 2 h	1.356	15.5	0.13	0.16
110 °C, ^a 5 h	1.365	19.6	0.19	0.20
125 °C, ^a 18 h	1.375	25.0	0.25	0.26
150 °C, ^a 18 h	1.379	26.4	0.27	0.28
175 °C, ^a 18 h	1.382	30.0	0.29	0.31
200 °C, ^a 18 h	1.392	34.4	0.35	0.36

^a Crystallinity calculated by density for m-PE, $\rho_a = 0.855$ g cm⁻³, $\rho_c = 0.999$ g cm⁻³; Ref. [25]. Crystallinity calculated by density for PET, $\rho_a = 1.335$ g cm⁻³, $\rho_c = 1.515$ g cm⁻³; Ref. [26]. Heat of fusion of PE at 298 K: $\Delta H_f^0(298) = 243.8$ J g⁻¹; Ref. [25]. Heat of fusion of PET at 375 K: $\Delta H_f^0(375) = 96.0$ J g⁻¹; Ref. [27]. <http://funnelweb.utcc.utk.edu/~athas/databank/phenylen/pet/petcalam.html>, <http://funnelweb.utcc.utk.edu/~athas/databank/phenylen/pet/petcalcr.html>.

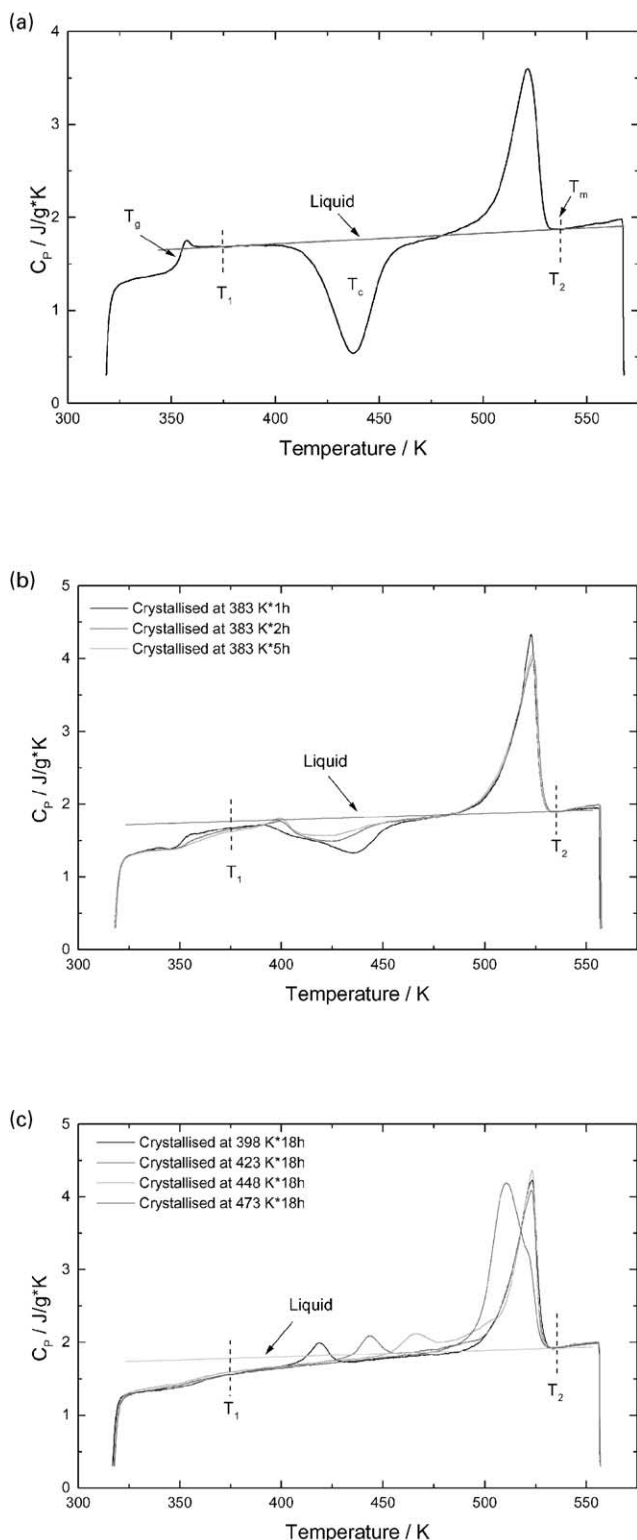


Fig. 4. (a) DSC analysis of amorphous polyethylene terephthalate along with the amorphous specific heat temperature dependence extrapolated from post- T_g temperature region. (b) DSC analysis of PET crystallised at 383K for different periods along with the amorphous specific heat temperature dependence derived from a quenched PET sample. (c) DSC analysis of PET crystallised for 18 h at different temperatures along with the amorphous specific heat temperature dependence derived from a quenched PET sample.

Table 2

Residual enthalpies and measured fractional crystallinities of amorphous PET

Sample	Residual enthalpy (J g^{-1})	Fractional crystallinity
1	-1.7	-0.018
2	-0.91	-0.009
3	2.3	0.024
4	1.9	0.019
5	-1.9	-0.020
6	2.8	0.029
7	3.7	0.038
8	-1.2	-0.012
9	-0.03	-0.000
10	-0.5	-0.005
Average		0.004 ± 0.020

smaller recrystallisation exotherm than previously observed with the amorphous samples. It was not possible in these samples to define the amorphous specific heat dependence with temperature either from the post- T_m dependence for reason discussed above or from the post T_g dependence since the materials were partially crystalline. Therefore, the specific heat–temperature dependence of amorphous samples were separately determined and used to evaluate ΔH_R of Eq. (5). The fractional crystallinity was then determined from the residual enthalpy of fusion at 375 K.

PET was also crystallised at different temperatures from 398 to 473 K for 18 h and the DSC thermal response with temperature is shown in Fig. 4c. Multiple melting points were observed with the lowest endotherm about 20 K above the crystallisation temperature and the temperature corresponding to the last trace of crystallinity almost constant and independent of crystallisation temperature. This has been attributed to the melting of lamellae produced on heating [29,30]. The same amorphous specific heat–temperature dependence as determined in Fig. 4b was used and the degree of crystallinity was obtained as outlined above. These results are listed in Table 1 and compared with the weight fraction crystallinity as measured by density. There is excellent agreement within experimental error between them.

5. Conclusions

The measurement of the degree of crystallinity in polymers by DSC has been reviewed. Since crystallisation, partial melting, annealing, recrystallisation and complete melting occur during the heating of the sample to the melting point the degree of crystallinity changes. The procedure of measuring the degree of crystallinity of the sample from the First Law method is valid and it measures a fractional crystallinity which compares favourably with that determined by other methods. Great care must be taken in selecting the specific heat temperature dependence of the liquid around which the specific heat response of the sample

with temperature is used as the baseline for integration. Degradation and volatile production from the polymer in the melt or on partially crystalline samples prior to heating negates the use of a specific heat baseline derived from the sample above the melting point or close to the glass transition. Instead the specific heat temperature dependence must be determined separately either from amorphous samples, or from the literature.

By using the First law method, the initial fractional crystallinity of m-PE and PET have been measured and found to be consistent with values determined by density at ambient temperature.

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