Journal of Thermal Analysis and Calorimetry, Vol. 66 (2001) 197–207

ANALYSIS OF CALORIMETRIC CURVES DETECTED DURING THE POLYMORPHIC TRANSFORMATION OF ISOTACTIC POLYBUTENE-1

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Abstract

Multiple endotherms detected on heating melt-crystallized *i*-polybutene-1 (PBu-1) are associated to the polymorphic transformation from the tetragonal (Form II) to the hexagonal modification (Form I). During this transformation, a progressive increase of the intensity of the high temperature endotherm, at the expenses of that pertaining to the low temperature one, is observed in DSC heating curves. Depending on molecular characteristics of the constituent chains and crystallization conditions, the two endotherms may exhibit some extent of superposition. In these cases, a reliable procedure to analyze the whole thermal curve must be found and adopted in order to follow the progress of the transformation in quantitative terms.

The same set of thermal curves, detected after various ageing times of melt-crystallized *i*-PBu-1, has been analyzed according to four different approaches. Comparison of the results shows that, with the exception of the analysis based on the 'partial area' routine, available to most instruments, all methods lead to equivalent results. The simplest approach, based on the mass balance during structural transformation, should be preferred whenever constant overall degree of crystallinity can be assumed throughout the whole process.

Keywords: DSC analysis, *i*-polybutene-1, kinetics, polymorphic transformation

Introduction

Multiple endotherms are quite common in the melting curves of semicrystalline polymers and their presence has been attributed to various origins. Most often, complex thermal curves have been associated to melting and re-crystallization phenomena during heating of thin and highly defective metastable crystalline lamellae [1–3]. However, melting of crystals with different morphologies [4–6] or structures [7–9] were also considered as possible origins for the appearance of more than one peak in the thermal curve. A detailed understanding of the phenomenon usually requires several calorimetric experiments, carried out at different heating rates, and also some independent information obtained by means of alternative experimental tools, such as X-ray scattering, spectroscopy, electron microscopy, etc.

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The quantitative interpretation of the thermal curve is particularly difficult when a continuous evolution of morphology takes place in the experimental time scale of thermal analysis since almost no data are available to describe the kinetics of recrystallization. Much simpler is to extract reliable information when multiple endotherms can unambiguously be attributed to melting of crystals with different structures already present in the specimen. This is the case of PBu-1, a polymorphic polyolefine that is known to exist in several crystal modifications [10–17]. Among them, only Forms II and I have been detected in melt crystallized samples in quiescent conditions. A tetragonal unit cell [11, 12] characterizes Form II and it is the kinetically favored modification obtained by melt crystallization. Upon ageing at room temperature, it slowly transforms into the more stable hexagonal modification, Form I, [10, 14] that exhibits a high crystalline density and a melting temperature about 10°C higher than that of Form II.

The kinetics of II→I transformation has been studied in detail in several experimental investigations. By using various techniques, it has been demonstrated that the polymorphic transformation occurs in a wide temperature range, form T_g, at about –25, up to about 60°C [18], with the rate showing a maximum between 20 to 40°C [12, 14, 15, 18–21]. It is also well known that the rate of transformation is affected by molecular characteristics of the material as well as by crystallization and ageing conditions. Hydrostatic pressure [12, 14, 16] and applied stresses or molecular deformation [20, 22–25] have been shown to strongly accelerate the structural transition, leading to full conversion in few hours. The effect of some additives on the kinetics of the transformation has also been reported [13, 15, 26]. A role on the rate of crystal–crystal transition is also played by molecular characteristics, such as molecular mass, microstructure and composition. Foglia [15] and Schaffhauser [27] claimed that the transformation rate increases on decreasing chain length while other authors reported that Form I develops at higher rate in polybutene-1 copolymers and in samples with lower steric order [28–30]. These observations suggest that low overall degree of order and inclusion of defects into the crystalline lattice favor the formation of the most stable polymorph.

Various experimental techniques have been used to study this transformation: from density measurements [18, 20] to WAXS [12, 22], from IR spectroscopy [20, 31, 32] to thermal methods [14, 31]. Among them, being fast and precise, thermal analysis is the most convenient one. However, since the difference between the melting temperatures of the two crystalline modifications is of the order of 10–15°C, melting curves often exhibit partial superposition. This implies that the recorded signal must be deconvoluted in its separate contributions to obtain a reliable evaluation of the extent of transformation from the thermal curves.

In this paper, we compare the outcome of four different approaches to analyze the same set of thermal curves obtained in a series of experiments at different ageing times.

Materials and techniques

The molecular characteristics of the five isotactic polybutene-1 homopolymers that have been investigated are reported in Table 1. De Clippeleir of Montell Polyolefines (Louvain-la-Neuve, Belgium) kindly provided the samples. PBu-1 films, about 300 μm thick, were prepared by compression molding in a Carver Press at 180°C followed by quenching in cold water. Several flat disks, weighing 5.0±0.2 mg, were punched out from the pressed films and placed into aluminum DSC pans. Samples were then submitted to a standardized thermal treatment to assure that each specimen experienced the same thermal history. The samples were firstly transferred into an oven at 180° for 5 min in order to obtain a fully relaxed melt and then they were crystallized by dropping them into small test tubes immersed in a thermostatic bath at 20°C. Under these conditions, most of the crystallization takes place during cooling. This has been ascertained by placing a small thermocouple into a film of comparable thickness sandwiched between two thin aluminum foils and submitted to the same temperature history. The temperature transient, recorded by a fast acquisition device, exhibits a clear quasi-isothermal plateau at about 50°C, indicating a substantial development of crystallinity at temperatures higher than ageing temperature at which the sample is held during polymorphic transformation. At various times, from few minutes up to two weeks, samples were removed from the crystallization bath at 20°C and submitted to thermal analysis. A Perkin Elmer DSC 7, calibrated with high purity indium and benzoic acid and operating under a purge of dry nitrogen, was used to study the melting behavior of aged samples. DSC traces were recorded between 30 and 150°C at a heating rate of 20°C min^{-1}.

Table 1 Molecular characteristics of isotactic-polybutene-1 samples

Sample code	Mass average molar mass	Fraction of isotactic pentads/%
PBu 110	850.000	83.1
PBu 200	525.000	82.7
PBu 300	295.000	81.7
PBu 400	177.000	79.5
PBu 800	116.000	79.5

Analysis of data

Four different approaches have been used to apportion the recorded curves between the melting transition of the two crystal populations and to evaluate the progress of the polymorphic transformation. Due to the adopted crystallization conditions, it can safely be assumed that the overall degree of crystallinity, i.e. the sum of the crystallinities in Form I and II does not change upon ageing:

$$x(t)=x_{\mathrm{II}}(t)+x_{\mathrm{I}}(t)=x_0=\text{const.} \tag{1}$$

If this assumption holds true, the time-dependent degree of polymorphic transformation is given by:

$$\varepsilon(t)=\frac{x_{\mathrm{I}}(t)}{x_{\mathrm{I}}(t)+x_{\mathrm{II}}(t)}=\frac{x_{\mathrm{I}}(t)}{x_0} \tag{2}$$

Partial areas

The first method is similar to that used by Rubin [21], and it is based on the application of the software enabling one to calculate partial areas of DSC traces. It calculates the fractional area of the first peak under the recorded curve, $F(T_x)$, as the integral of the detected signal, $Q_{\exp}(T)$, from some fixed initial temperature, T_0, to the temperature of interest, T_x, divided by the full integral of the curve:

$$F(T_x)=\frac{\int_{T_0}^{T_x} Q_{\exp}(T)\mathrm{d}s}{\int_{T_0}^{T_e} Q_{\exp}(T)\mathrm{d}s} \tag{3}$$

where T_e corresponds to the temperature at which the signal returns to the base line. The amount of the two crystal forms is then calculated by converting the area of the peaks into enthalpy and by dividing this value by the melting enthalpy of the corresponding perfect crystals. This calculation method can safely be applied only if the endotherms related to melting of the different type of crystals are well separated and a T_x value, at which the intensity of the signal is zero or negligible, can be identified in the melting range. Otherwise, one needs to arbitrarily assume that the contributions of the two separated melting processes can be evaluated by drawing a vertical line from the curve to the baseline at some temperature between the two peaks. Lack of any better criterion suggests drawing this line in correspondence of the relative minimum

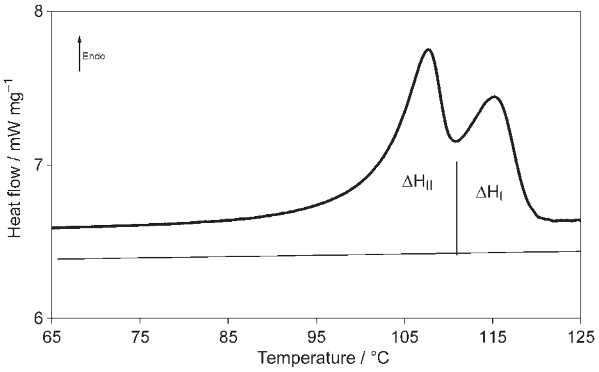

Fig. 1 Example of DSC curve showing multiple melting endotherms. PBu-1 aged 41 h at 20°C

of the curve as shown in Fig. 1. However, it should be noted that this procedure underestimates the major component when the intensities of the two peaks are appreciably different, i.e. at the beginning and at the end of the transformation. A further complication arises at the very end of the process, when the endotherm associated to melting of the small remaining fraction of Form II might be fully hidden by the overwhelming endothermic effect of Form I.

Simulation approach

This approach is based on the linear combination of DSC signals that are obtained by heating the samples immediately after crystallization or after a very long ageing time. In fact, in as-crystallized samples only the low melting endotherm, characterizing the kinetically favored tetragonal form, is present; on the other hand, in samples investigated after one month of ageing at 20°C all crystals have fully transformed into the high melting hexagonal modification.

Applicability of this method requires that the peak temperatures and the shapes of each endotherm do not depend on the extent of polymorphic transformation. As shown by the collection of melting curves reported in Fig. 2, the assumption that the peak maxima do not shift with ageing time is reasonably well fulfilled. At any temperature in the melting range, the recorded signal is assumed to be the weighed sum of the independent thermal effects associated to melting of the ensemble of crystals belonging to each crystal form:

$$Q_\varepsilon(T) = \varepsilon Q_\mathrm{I}(T)+(1-\varepsilon)Q_\mathrm{II}(T) \tag{4}$$

where $Q_\mathrm{I}(T)$ and $Q_\mathrm{II}(T)$ represent the temperature dependent signal measured on samples containing only the indicated type of crystals and $Q_\varepsilon(T)$ is the resulting intensity

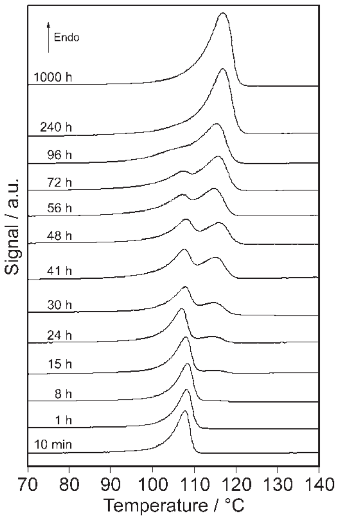

Fig. 2 Collection of DSC traces recorded at different ageing times at 20°C

of the simulated signal at an assigned degree of transformation, ε. From the knowledge of $Q_{\mathrm{I}}(T)$ and $Q_{\mathrm{II}}(T)$ one can easily produce the whole set of simulated thermal curves from $\varepsilon=0$ to $\varepsilon=1$.

Next step requires the comparison of the experimental melting curve, recorded after a given ageing time, with the series of simulated curves. By visual examination, a rather narrow range of possible values of ε, providing simulated curves that fairly match the experimental one, can easily be identified. Fine tuning is then performed by finding the value of ε corresponding to the simulated curve that minimizes the difference between the recorded and the calculated DSC signal over the whole range of the melting transitions:

$$\sum_{\mathrm{T_i}}^{\mathrm{T_e}}[Q_{\varepsilon}(T)-Q_{\mathrm{exp}}(T)]^2=\mathrm{min} \tag{5}$$

This last step can conveniently be accomplished by using common spreadsheets.

It should be observed that this method of data analysis provides results that are less subjective, in comparison with those obtained by the method of partial areas; however, the optimization procedure is lengthy and critically dependent even on small shifts in the peak temperature of both endotherms.

Deconvolution by PEAK-FIT program

The application of a curve deconvolution program has been attempted to quantitatively evaluate the contribution of individual melting processes of the two crystal forms to the recorded DSC signal. Several options are available to deconvolute curves obtained by spectroscopic and chromatographic techniques; however, to our knowledge, no such software has yet been specifically developed to treat thermal data obtained by differential thermal analysis or differential scanning calorimetry. To analyze our multiple endotherms, it turned out practical to adopt the PEAK-FIT V4 program that is usually applied to deconvolute complex IR spectra.

The non-symmetric peaks characterizing the melting endotherms of a distribution of crystals with different sizes and degree of perfection can easily be handled by using exponentially modified Gaussian functions to describe the temperature dependence of the intensity of measured signal:

$$Q_{\mathrm{exp}}(T)=\frac{A}{2\beta}\exp\left(\frac{\alpha^2}{2\beta^2}+\frac{T_{\mathrm{M}}-T}{\beta}\right)\left[\mathrm{erf}\left(\frac{T-T_{\mathrm{M}}}{\sqrt{2}\alpha}-\frac{\alpha}{\sqrt{2}\beta}\right)+\frac{\beta}{|\beta|}\right] \tag{6}$$

where A is the area of the peak, T_{M} is the position of the peak maximum in the temperature scale, α the peak width at the inflection point and β the peak distortion.

An example of the quality of the fit that can be obtained by this method is shown in Fig. 3, where the actual thermal curve and its components are drawn. It can be observed that the modified Gaussian functions account fairly well for the much less steep dependence of the signal on the low temperature side of the peaks. Optimization

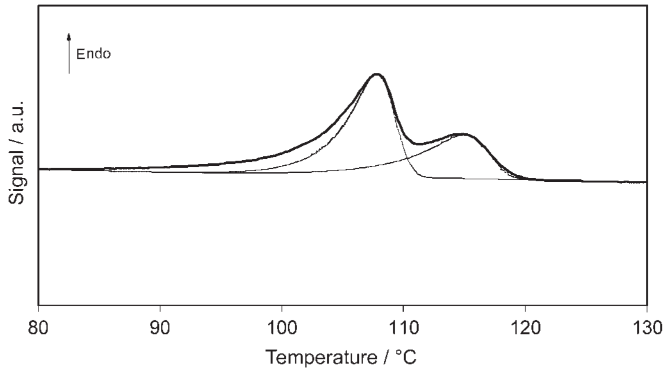

Fig. 3 Deconvolution of the DSC curve obtained by PEAK-FIT V4

of the fit provides the values of individual components with a correlation coefficient always higher than 0.995.

Total melting enthalpy

In this last method of data analysis, the individual contributions of the two melting endotherms do not need to be separated and the progress of the transformation as a function of ageing time can be obtained from the direct measurement of the whole, bimodal, endotherm. If, according to Eq. (1), a constant total degree of crystallinity, $x_0=x_I+x_{II}$, is preserved during aging and melting of the two crystal populations are independent processes

$$\Delta H_{TOT}(t)=\Delta H_I(t)+\Delta H_{II}(t)=w[x_I(t)\Delta H_I^0+x_{II}(t)\Delta H_{II}^0] \quad (7)$$

it can easily be shown that the relation between the degree of transformation, $\varepsilon(t)=x_I(t)/x_0$, and the measured intensity of the total endotherm, $\Delta H_{TOT}(t)$, reads:

$$\varepsilon(t)=\frac{\dfrac{\Delta H_{TOT}(t)}{\Delta H(t=0)}-1}{R-1} \quad (8)$$

where R is the ratio between ΔH_I^0 and ΔH_{II}^0, the melting enthalpy of ideal crystals in Forms I and II, respectively, $\Delta H(t=0)$ is the heat of melting measured at zero ageing time, i.e. on samples containing only crystals in Form II.

The precise values of melting enthalpies of the ideal crystals of both polymorphs are not known. A critical examination of literature data [21, 26, 33–35] suggests that ΔH_I^0 is between 110 and 150 J g^{-1}, while the corresponding value for the less stable modification has been reported in the range 60–110 J g^{-1}. In order to select the best value to be adopted in our calculations, PBu-1 samples of different molecular mass were crystallized and aged for one month at 20°C. These samples had a degree of crystallinity, as determined by density gradient method, of 0.51±0.02 and their measured melting enthalpy, calculated from the single high temperature peak of the thermal curve, was 72±2 J g^{-1}. From these results, the value of 141±10 J g^{-1} is obtained for the melting enthalpy of ideal crystals in Form I. Several experiments, in which the melting enthalpy was measured in as-crystallized polybutene-1 samples in form II, gave a value of 31±2 J g^{-1}. Therefore, if the amount of crystallinity does not change during transformation, ΔH_{II}^0 should be in the range 58–65 J g^{-1}, corresponding to R values between 2.1 and 2.6. Actual data, collected from several samples at various ageing times, suggest that the best value for R is 2.27±0.03. This value being in substantial agreement with R=2.12 adopted by Rubin [21].

Results and discussions

The time-dependent degree of polymorphic transformation at 20°C, calculated from the melting curves of melt crystallized samples of isotactic polybutene-1 (PB 200) according to the four different approaches, is shown in Fig. 4. Similar results have also been obtained with all other investigated homopolymers. In agreement with published results [20, 21, 26, 36, 37], appearance of the high temperature endotherm is detected after few hours; then a gradual increase of Form I is detected and the process reaches its completion in about two weeks.

All approaches for the analysis of the melting endotherms provide equivalent results in the initial stages of the transformation. However, on increasing ageing time, the method of partial areas appreciably underestimates the amount of Form I. When the residual Form II drops below 20%, its melting endotherm is hidden by the low temperature side of the high temperature peak and, due to the much lower value of ΔH_{II}^0, cannot longer be detected. This produces an apparent jump of the evaluated degree of transformation. On the other hand, deconvolution of thermal curves by means of simulation method and PEAK-FIT program lead to the same values of $\varepsilon(t)$ calculated from the total enthalpy method over the whole process of transformation. The

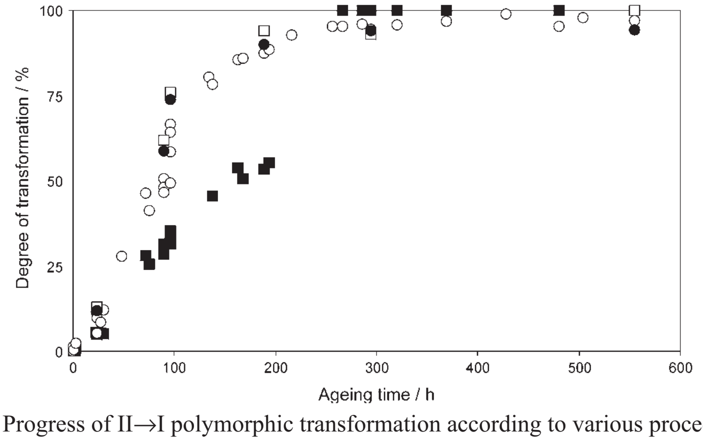

Fig. 4 Progress of II→I polymorphic transformation according to various procedures of data analysis; ■ – partial areas, □ – simulation, ● – Peak-Fit V4, o – total melting enthalpy

total enthalpy method should be preferred since it does not require any arbitrary assumption on the equation describing the shapes of melting endotherms and it can be applied even if some fluctuation in the value of peak temperatures is recorded.

However, it should be noted that notwithstanding our attempts to perform experiments in very controlled conditions, and having always adopted the same criteria to draw the base lines of the thermal curves, some degree of data scattering was obtained. In the worst cases, the degree of transformation estimated in samples submitted to the same thermal history differs of about 10%. Such relatively large differences cannot be attributed to poor reproducibility of thermal analysis. Instead, since it is well known that the rate of transformation is strongly dependent on stresses acting on crystalline lamellae [12, 20, 22–25], we suggest that the observed differences might be due to fortuitous mechanical stresses applied during handling of DSC pans containing the molten polymer. Also uncontrolled thermal stresses, originated during cooling to the ageing temperature, may play a role on the nucleation of daughter crystalline phase.

The total enthalpy method has been applied to study the role of the average molar mass on the kinetics of II→I transformation at 20°C. The transformation half time, corresponding to $\varepsilon(t)=0.5$, was interpolated from the curves drawn through the large set of data acquired for each sample. As shown in Fig. 5, the kinetic rate constant is barely affected by chain length and no clear trend can be observed on increasing molar mass. The average value of the transformation half time is about 70 h and its fluctuation around the mean value corresponds to less than 10% of the time needed to reach completion of the transformation. Foglia [15] reported that the rate of the process decreases on increasing chain length; however, he made his experiments using samples with average molar mass below 100.000 and he did observe a gradual leveling off at high molecular masses. In addition, Schaffhauser [27] reported that large variations in the rate constant are associated with the degree of steric order along the chain: faster transformation was found for less stereo-regular polymers. In order to compare kinetic data, the effect of individual molecular parameters should be taken into account. Unfortunately, polybutene-1 samples in which one of the chain characteristics is variable, while the other is strictly constant, were not available to us, neither they were available to Foglia and Schaffhauser. However, the high molar mass

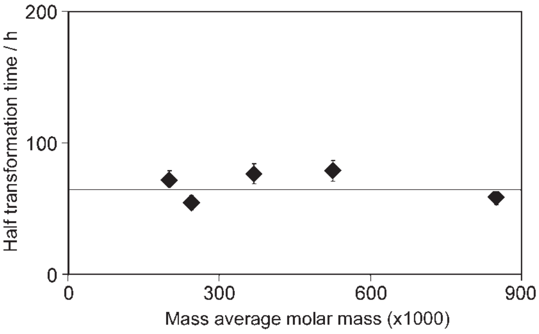

Fig. 5 Dependence of rate of polymorphic transformation on polymer molar mass

and the rather constant tacticity of our samples justifies the apparent disagreement between our results and those reported earlier [15, 27, 31].

Conclusions

Thermal analysis is a powerful technique to investigate the kinetics of the II → I polymorphic transformation in isotactic polybutene-1. Even if appreciable superposition of the melting endotherms of parent and daughter crystalline phases appears in DSC curves, several methods can be applied to deconvolute the total heat effect in its individual components and to obtain kinetic data. Four different methods to extract the contribution of Form I and Form II from superposed multiple endotherms have been applied. Except the one based on partial areas, all methods provide comparable results. If the degree of crystallinity can be assumed constant through the transformation, the simple and less subjective approach based on the measurement of the total melting enthalpy as a function of ageing time can be applied to obtain accurate data. This approach to data analysis has been applied to show that the rate of transformation is independent of the polymer chain length.

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