On the Determination of the Enthalpy of Fusion of α-Crystalline Isotactic Polypropylene Using Differential Scanning Calorimetry, X-Ray Diffraction, and Fourier-Transform Infrared Spectroscopy: An Old Story Revisited

Franz J. Lanyi, Nicolai Wenzke, Joachim Kaschta, and Dirk W. Schubert

The crystallinity determination of polymers using differential scanning calorimetry (DSC) is a standard procedure in industrial and university research. Its value strongly depends on the enthalpy of fusion, which cannot be determined directly using DSC, but must be calibrated using external methods such as X-ray diffraction (XRD) or density measurements. In addition, the determination of the enthalpy of heat of fusion is not trivial and thus error-prone; hence, values from 60 to 260 J g\(^{-1}\) are quoted for polypropylene in the literature. It is therefore of great relevance to devise a consistent method to determine the heat of fusion. To determine the heat of fusion for polypropylene, a sample set with a broad range of crystallinities is produced using cooling rates between 1 and \(\approx 3500\) K min\(^{-1}\). The melting enthalpy of the samples is determined using DSC measurements. The determination of the melting enthalpy based on XRD measurements is discussed in detail, validated using Fourier-transform infrared spectroscopy (FTIR), and compared with values quoted in the open literature. Although two different approaches are used to determine the enthalpy of fusion, a value of 170 ± 3 J g\(^{-1}\) is determined.

1. Introduction

Differential scanning calorimetry (DSC) is one of the most important methods for determining the crystallinity of polymers and is used by universities as well as for industrial research.\(^1\)–\(^3\) The degree of crystallinity is determined by measuring the amount of heat required to melt a given polymer (also called enthalpy of melting \(\Delta H_m\)). This value is divided by the heat required to melt a sample with a crystallinity of 100% (also called heat of fusion \(\Delta H_m^{100}\)) to obtain the degree of crystallinity \((X_c)\)\(^4\)

\[
X_c = \frac{\Delta H_m}{\Delta H_m^{100}} \tag{1}
\]

Therefore, the heat of fusion and, consequently, its determination strongly influence the value of \(X_c\). As a result, the crystallinity of a polymer can be greatly over- or underestimated from DSC measurements if an incorrect value for enthalpy of fusion is used.

Equation 1 constitutes a linear relationship between \(\Delta H_m\) and \(X_c\) and therefore requires one value for each \(\Delta H_m\) and \(X_c\) of a given sample to calculate \(\Delta H_m^{100}\). However, more data points ranging over a broad regime of crystallinities allow a more precise determination of \(\Delta H_m^{100}\) and thus provide higher statistical significance. To determine \(\Delta H_m^{100}\), the samples have to be measured using DSC, and a calibration-free method for crystallinity determination has to be used. Any error in either enthalpy of melting or crystallinity will amplify the error in the value for heat of fusion. Such errors may arise from methodological shortcomings such as a too small sample set or single-point measurements. Other errors may stem from the preparation of the calibration samples used, e.g., crystallinity gradients across the sample, or even problems with data evaluation, such as an imprecise baseline for the determination of \(\Delta H_m\).

A review of the published literature on values for \(\Delta H_m^{100}\) for PP focussed on the sample set used, including information on isotacticity, ethylene content, or molar mass distribution, showed that the values range widely and are incomplete in most cases. The determination of the enthalpy of fusion of PP is a continuing topic of research since the first publication in 1957. Most studies were published during the 1960s and the early 1970s, reporting values between 138\(^6\) and 221 J g\(^{-1}\).\(^6\) The degree of crystallinity was usually determined using wide-angle X-ray scattering (WAXS)\(^7\) or density measurements.\(^8\)–\(^10\) In other studies, Raman spectroscopy was used.\(^11\)–\(^13\) Although more than 20 different values for the heat of fusion have been published (see reviews by Wilkinson and Dole\(^12\) and Wunderlich\(^14\)), the values
differ greatly, due to the methodology used or the calibration sets being too small. For this reason, there is still a great need for a reliable and consistent determination of the heat of fusion.

For most papers published in the recent literature, the value 207 ± 5 J g⁻¹ for the heat of fusion ΔH⁺° of isotactic polypropylene (i-PP) has been used, which was first determined by Gee and Melia[13] in 1970 and subsequently propagated to numerous publications, mostly without quoting the original publication but referencing other papers.[16–19] In the study by Gee and Melia,[13] it should be seen critically that single-point measurements of only two different samples were used to determine the heat of fusion. Furthermore, in this article, the choice of baseline to determine the melt enthalpy ΔHm is highly questionable, as the baseline of the solid and the molten state do not meet when extrapolated. This is due to the baseline shift between the two regimes, which contributed to the exaggerated value of the melting enthalpy. Compared to currently used techniques, such as linear- or spin-type baselines, this yields higher values for the enthalpy of melting resulting in an overestimation of the heat of fusion ΔH⁺°. Wilkinson and Dole compiled a literature review, in which values from 60 to 260 J g⁻¹ were cited.[13] They also determined the heat of fusion to be 146 J g⁻¹ using density measurements to determine the degree of crystallinity. More recently, another value has been reported by Li et al.[20] They determined the heat of fusion of an α-crystalline polypropylene as 177 J g⁻¹, again using density measurements to determine the crystallinity of PP.[8] Only two samples with almost the same degree of crystallinity were used in this study to determine the heat of fusion, which undermines the reliability of the results. Wunderlich[14] reported another value for the heat of fusion, namely, 166 ± 18 J g⁻¹ by merely calculating the average heat of fusion from five different publications,[5,10,13,20,21] which all used single-point measurements of different polypropylene grades without supplying detailed information on them. This approach puts the validity of the results into question.

Contrary to the current state of the literature, this work shows a novel approach, in which the heat of fusion of an α-crystalline polypropylene is determined using samples that cover the entire range of experimentally obtainable crystallinities by utilizing cooling rates between 1 and 3500 K min⁻¹. All measurements were carried out on a well-defined and characterized polypropylene sample to exclude influences of molecular weight, branching, polydispersity, or copolymers. The crystallinity was determined and evaluated by DSC, X-ray diffraction (XRD), and Fourier-transform infrared spectroscopy (FTIR) to obtain a consistent and reliable value for the enthalpy of fusion. Furthermore, recrystallization phenomena in rapidly cooled samples are discussed in depth using literature examples to put the results into context. This study represents a methodical strategy to correctly determine ΔH⁺° and may in the future provide a basis for determining the heat of fusion of other polypropylene or polymers in general.

2. Experimental Section

2.1. Materials and Molecular Characterization

For this study, an i-PP was used, which was distributed under the trade name Moplen HP561R and was kindly provided by LyondellBasell. It was a spingrade polypropylene, commonly used for the production of fibers and nonwovens.[22,23] The polypropylene had a melt flow index (MFI) of 25 g (10 min)⁻¹ at 230 °C/2.16 kg, a weight average molar mass Mw of 185.9 ± 2.1 kg mol⁻¹, and a polydispersity of 4.3 ± 0.1. All molecular parameters were analyzed by high-temperature size exclusion chromatography on an Agilent PL-GPC-220 coupled with a multilayer light-scattering device Dawn Eos from Wyatt Technology. The values reported here were mean values and standard deviations of four different measurements. The molar mass distribution is shown in Figure 1. To our knowledge, no nucleating agents were added to the polypropylene that was used.

2.2. X-Ray Diffraction

XRD measurements were carried out on a Philips Theta-Theta goniometer with CuKα radiation between 10° and 40° and a step width of 0.01°, each step being measured for 10 s. Prior to evaluation, the background of all data was adjusted with a correction parameter of 0.025 using Bruker’s EVA program.

In the XRD measurement, the degree of crystallinity XC was determined by the ratio of the area of the peaks proportional to the crystalline part and the total area under the curve[24] (Equation (2)).

\[
X_C = \frac{A_{\text{crystalline}}}{A_{\text{crystalline}} + A_{\text{amorphous}}}
\]

(2)

The amount of crystalline and amorphous phases of the samples was determined by a deconvolution method based on the fit of modified Gaussian peak functions (Equation (3))[25] to the crystalline peaks and a bi-Gaussian peak function (Equation (4))[26] for the amorphous phase.

\[
y(2θ) = 4λe^{-4ln(2)(θ − x)^2} \frac{W}{\sqrt{4\ln(2)}}
\]

(3)

![Figure 1](image-url)  
Figure 1. Molar mass distribution function of the i-PP used in this study.
\[ y(2\theta) = h \cdot e^{-0.5\left(\frac{w_1}{w_2}\right)^2} \text{ for } (2\theta < x_c) \]
\[ y(2\theta) = h \cdot e^{-0.5\left(\frac{w_1}{w_2}\right)^2} \text{ for } (2\theta \geq x_c) \]

The sample with the highest degree of crystallinity was evaluated first, as the amorphous halo and crystalline peaks were most pronounced for this sample. All parameters characterizing the peak shape of the amorphous halo (widths \(w_1\) and \(w_2\) and the center position \(x_c\)) of the sample with the highest crystallinity, except the peak height \(h\), were kept fixed and then used for the other samples. The implementation of the fit was achieved using a least squares algorithm by the program Origin. The coefficient of determination was between 0.948 and 0.983 for all evaluated samples resulting in a typical error of \(\pm1\%\) in crystallinity, which is comparable to other publications. Other evaluation methods, e.g., the use of a simple Gaussian peak function for the amorphous halo or the use of a simultaneous fitting approach (as described in a publication by La Carrubba et al.), yielded very comparable fitting results and calibration curves. For further evaluation, reflections at \(2\theta = 14.1^\circ, 16.9^\circ, 18.6^\circ, 21.2^\circ, 22.1^\circ, 25.5^\circ,\) and \(28.5^\circ\) were assigned to the \(\alpha\)-monoclinic phase and reflections at \(2\theta = 14.5^\circ\) and \(21^\circ\) to the mesomorphic phase. A \(\beta\)-phase was not considered as peaks correlating with the \(\beta\)-phase were not found for any of the samples. Furthermore, the \(\beta\)-phase will usually develop only in fiber-spinable polypropylenes.

2.3. Differential Scanning Calorimetry

All DSC measurements were carried out on a DSC Q 2000 differential from TA instruments. For each sample, one heating run under nitrogen atmosphere (flow of 20 mL min\(^{-1}\)) was conducted from \(-40\) to \(200^\circ\)C at the rate of \(10\) K min\(^{-1}\).

The melt baseline was extrapolated toward the lower temperature, resulting in two endothermic and one exothermic peak for the mesomorphic samples and one peak that ranged from about \(100\) to \(170^\circ\)C for the \(\alpha\)-crystalline samples (see also Figure 2).

2.4. Fourier-Transform Infrared Spectroscopy

All FTIR measurements were carried out on a Nicolet 6700 FTIR spectrometer at a temperature of \(23^\circ\)C. Each measurement was an average of 128 scans at a resolution of \(0.48\) cm\(^{-1}\). Since all peaks used in this study, which were needed to determine the crystallinity of polypropylene, were in a spectral range between \(900\) and \(1050\) cm\(^{-1}\), the spectra were recorded within a wave number range of \(1400-700\) cm\(^{-1}\) only to reduce the measurement time. The data points shown in this study represent the mean value and the standard deviation of three measurements at three different spots of a single sample. For measurements in attenuated total reflection mode (ATR)-FTIR, a diamond and a germanium single bounce crystal were used. Both crystals had an angle of reflection \(\theta = 42^\circ\). For a refractive index \(n_{\text{Dia}} = 2.4\) of diamond and \(n_{\text{PP}} = 1.49\) of polypropylene, Equation (5)[24] gave a penetration depth of \(2.55\) \(\mu\)m at a wavenumber of \(980\) cm\(^{-1}\). The corresponding penetration depth for germanium \((n_{\text{Ge}} = 4.0)\) was \(0.7\) \(\mu\)m. In this study, the IR-irradiated sample volume of both crystals was considered as a near-surface region. For all measurements, the baseline and ATR penetration depth were corrected using Thermo Fisher’s OMNIC 9 program.
\[ d_p(\lambda)[\mu m] = \frac{10^4 \cdot \lambda[mm]}{2n_{\text{crystal}} \cdot \pi \cdot \sqrt{\sin^2(\theta) - \left( \frac{n_{\text{sample}}}{n_{\text{crystal}}} \right)^2}} \]

(5)

It had already been shown repeatedly in the literature that the peak height at 998 cm\(^{-1}\) \((h_{998})\) of an FTIR spectrum of polypropylene was proportional to the degree of crystallinity.\(^{[29-31]}\) Furthermore, it was demonstrated that the peak height at 973 cm\(^{-1}\) \((h_{973})\) correlated linearly with the irradiated volume.\(^{[32-34]}\) Hence, the peak ratio \(h_{998}/h_{973}\) was used as a measure of crystallinity, which offered the possibility to determine the degree of crystallinity nondestructively via FTIR.

\[
X_c \sim \frac{h_{998}}{h_{973}}
\]

(6)

A previous publication had already demonstrated the proportionality of the peak ratio \(h_{998}/h_{973}\) and the degree of crystallinity \((X_c)\) in polypropylene.\(^{[35]}\) The peak height of both peaks was determined by initially drawing a linear baseline determined by the points at 1025 and 950 cm\(^{-1}\). In a second step, the height between the baseline and the highest measured signal value in the range 960–985 cm\(^{-1}\) (for the band at 973 cm\(^{-1}\)) and in the range 985–1005 cm\(^{-1}\) (for the band at 998 cm\(^{-1}\)) was determined.

### Table 1. Overview of the manufacturing methods used for sample preparation for the calibration set.

| Cooling method            | Cooling rate          |
|---------------------------|-----------------------|
| Salt–ice–water + stirring  | \(\approx\)3500 K min\(^{-1}\) |
| Salt–ice–water            | \(<\)3500 K min\(^{-1}\) |
| Salt–ice–water + 50 °C annealing | \(<\)3500 K min\(^{-1}\) + 50 °C tempering |
| DSC                       | 20 K min\(^{-1}\)     |
| DSC                       | 1 K min\(^{-1}\)      |

2.5. Sample Preparation and Calibration Procedure

To obtain reproducible calibration samples, the polypropylene was pressed into thin films with a uniform thickness of \(\approx 280 \mu m\) using a Vogt Labopress 200 T hot press at 240 °C under vacuum. The samples were heated for 1 min without pressure and for 2 min with a pressure of 10 and 200 bar, respectively. The samples were then cooled between two ceramic plates to obtain a uniform surface structure. From these films, samples with a diameter of 4 mm were punched out and put in T Zero DSC crucibles (TA Instruments). These crucibles have the advantage that they can be sealed both air and watertight and provide perfect contact and thus good heat conduction to the top and bottom of the sample, thus enabling uniform, rapid heating and cooling of the specimen. To cover the broadest possible range of achievable crystallinities, the samples were either treated using DSC or via a quenching procedure. Defined low cooling rates were achieved by heating the samples to 200 °C and cooling them at rates of 1 and 20 K min\(^{-1}\) using DSC. To achieve high cooling rates, the samples were first heated to 200 °C in a hot-air oven for 5 min and then quenched in a mixture of water, ice, and salt with and without stirring. The quenching process leads to cooling rates of \(\approx 3500\) K min\(^{-1}\) (estimated using an approach described in the study by Böckh and Wetzel\(^{[36]}\)). After quenching, one sample was tempered at 50 °C for 1 h to force postrystallization in the range of 5–10%.\(^{[11]}\) An overview of the experimental settings used to produce the calibration set is shown in Table 1.

After heat treatment, the samples were removed from the DSC crucibles and examined with ATR-FTIR at two penetration depths. This was done to ensure that the samples had not developed a crystallization gradient toward the surface that would prevent an accurate calibration procedure (Figure 3a). The samples were measured daily using ATR-FTIR to determine the evolution of crystallinity over time. Due to relaxation processes in the polymer, the degree of crystallization of strongly quenched samples may change even when stored at room temperature. For this

![Figure 3](image-url)
reason, all XRD measurements were carried out after a storage time of 48 h. After the XRD measurement, the samples were measured again using ATR-FTIR to detect possible postcrystallization during the XRD measurement (Figure 3b). To determine the enthalpy of fusion, the samples were then placed in DSC crucibles and measured using DSC.

3. Results

The crystalline phase of polypropylene may be found in the mesomorphic, α, β, or γ crystalline form. The α-crystalline form is the most stable, whereas the β- and γ-crystalline structures are metastable. The latter require special nucleating agents and processing conditions and do not occur in the polypropylene used for this study. The mesomorphic phase requires supercooling of the melt and shows a transition to the α-phase at around 50–80 °C.[1] Figure 4 shows the diffractograms of all samples from the calibration set. The XRD study showed that the samples cooled in the DSC at slow cooling rates and the tempered sample exhibited α-crystalline morphology, whereas both samples produced by the quenching process in ice water without tempering are mesomorphic.

Figure 2 shows the DSC curves of all samples used in the calibration set. The mesomorphic samples first showed a small endothermic peak of 2.7 J g⁻¹ between 30 and 70 °C. This peak is often associated with the melting of smaller crystalline structures.[19,37] The endothermic peak was followed by an exothermic peak between 75 and 120 °C, which is usually attributed to recrystallization phenomena and the transition from the mesomorphic to the α-crystalline phase.[180] and is ≈9 J g⁻¹ for the two mesomorphic samples shown here. Assuming that the endo- and exothermic peaks between 30 and 120 °C are associated with melting and recrystallization phenomena, the specific enthalpies would have to be added or subtracted from the main peak to describe the initial crystalline state determined with XRD.

Contrary to previous work, Caldas et al.[39] showed in an extensive study on the mesomorphic phase of i-PP that it is more realistic to assign the endothermic peak between 30 and 70 °C to a premelting transition that can occur before the recrystallization and is therefore not related to a change in crystallinity. This transition can include, for example, the expansion of the crystal in one or more dimensions. This assumption is based on the observations that the heat applied when melting strongly quenched polypropylene describes only about 23% of the energy required to melt all the microcrystals of the mesomorphic phase. Furthermore, it was concluded that the exothermic peak between 80 and 120 °C is probably due to an improvement of crystal perfection. Since the mesomorphic phase consists of micro- and intercrystalline regions within an α-crystalline structure, this transformation can be described as a kind of optimization of already existing α-crystalline parts to states of higher order. In the DSC curves discussed here, the exothermic peak is only present in samples with a mesomorphic crystal structure, supporting the hypothesis that the exothermic peak is rather a phase transition phenomenon than a recrystallization phenomenon.

Similar results were also shown by Zhao et al.[28] In their work, quenched mesomorphic i-PP was heated, whereas WAXD diffractograms were recorded simultaneously. It turned out that the mesomorphic phase transformed into the α-crystalline phase at temperatures of 85 °C and above. The increase in the α-crystalline phase was at the expense of the mesomorphic phase since the amorphous phase remained unchanged. A study by Nitta and Odaka also showed that quenched i-PP from 60 °C transformed from a mesomorphic to an α-crystalline structure, whereas the amorphous phase content remained unchanged.[40]

Based on the reported results, the DSC curves may be discussed using two different approaches. In the first approach, the enthalpies of the exo- and endothermic peaks before the main melting peak are subtracted and added to the main melting enthalpy, assuming that these are related to premelting and recrystallization phenomena. In the second approach, only the enthalpy of the main melting peak is discussed without subtracting the endothermic and exothermic peaks of the mesomorphic samples assuming that the effects causing these enthalpies are
mostly related to transformation phenomena leading to higher states of crystalline order and not leading to an increase or decrease in crystallinity.

Figure 5 shows the melt enthalpy as a function of the crystallinity determined via XRD. By fitting the data with a straight line through the origin, the melting enthalpy of a theoretically 100% crystalline polypropylene was determined.

\[ \Delta H_m = \Delta H_{m}^{100} \times \frac{X_c [\%]}{100\%} \]  

(7)

The fit yields a value of 171 ± 2 J g\(^{-1}\) for the enthalpy of fusion when merely using the main melting peak for the determination of the enthalpy of melting and a value of 166 ± 3 J g\(^{-1}\) for the approach when adding and subtracting the peaks from the main melting peak. Since the mesomorphic samples, which were stored for 60 min at 50°C, exhibit on the one hand an \(\alpha\)-crystalline structure and on the other hand a higher crystallinity, it may be assumed that amorphous parts of the polypropylene recrystallize and mesomorphic parts transform. Our results neither confirm nor disprove either one of the two hypotheses discussed earlier. However, it also becomes clear that the resulting heat of fusion is almost the same for both routes of evaluation. Therefore, the measurements strongly point to the average value for enthalpy of fusion for the \(\alpha\)-crystalline iPP used in this study to be 170 ± 3 J g\(^{-1}\).

The results we found are in accordance with the values of 166 and 177 J g\(^{-1}\) found by Wunderlich\(^{[14]}\) and Li et al.\(^{[8]}\) respectively. This confirmation may be by accident, as a more error-prone methodology was used in the previous works compared with this article where determination was based on a set of well-defined samples from the same material and highly reproducible measurements.

Since the determination of the correct enthalpy of melting \(\Delta H_m\) is not trivial for the case of rapidly cooled polypropylenes, additional FTIR measurements of the samples were carried out. As the peak at a wave number of 998 cm\(^{-1}\) in the FTIR spectrum of polypropylene disappears completely in the melt, whereas the peak at 973 cm\(^{-1}\) remains constant,\(^{[33]}\) it may be assumed that the peak ratio \(h_{998}/h_{973}\) equals 0 in the absence of crystallinity. Assuming that the peak ratio is proportional to the degree of crystallinity,\(^{[35]}\) it can be concluded that a linear fit of the peak ratio \(h_{998}/h_{973}\) can be used to describe the enthalpy of fusion if it is determined correctly

\[ \Delta H_m = k \times \frac{h_{998}}{h_{973}} \]  

(8)

If the data points deviate significantly from the straight line, the correct determination of the enthalpy of fusion would be questionable. Figure 6a shows that the linear fit using

\[ \Delta H_m = \Delta H_{m}^{100} \cdot \frac{X_c [\%]}{100\%} \]  

(9)

of the enthalpy of melting and a value of 166 ± 3 J g\(^{-1}\) for the approach when adding and subtracting the peaks from the main melting peak. Since the mesomorphic samples, which were stored for 60 min at 50°C, exhibit on the one hand an \(\alpha\)-crystalline structure and on the other hand a higher crystallinity, it may be assumed that amorphous parts of the polypropylene recrystallize and mesomorphic parts transform. Our results neither confirm nor disprove either one of the two hypotheses discussed earlier. However, it also becomes clear that the resulting heat of fusion is almost the same for both routes of evaluation. Therefore, the measurements strongly point to the average value for enthalpy of fusion for the \(\alpha\)-crystalline iPP used in this study to be 170 ± 3 J g\(^{-1}\).

The results we found are in accordance with the values of 166 and 177 J g\(^{-1}\) found by Wunderlich\(^{[14]}\) and Li et al.\(^{[8]}\) respectively. This confirmation may be by accident, as a more error-prone methodology was used in the previous works compared with this article where determination was based on a set of well-defined samples from the same material and highly reproducible measurements.

Since the determination of the correct enthalpy of melting \(\Delta H_m\) is not trivial for the case of rapidly cooled polypropylenes, additional FTIR measurements of the samples were carried out. As the peak at a wave number of 998 cm\(^{-1}\) in the FTIR spectrum of polypropylene disappears completely in the melt, whereas the peak at 973 cm\(^{-1}\) remains constant,\(^{[33]}\) it may be assumed that the peak ratio \(h_{998}/h_{973}\) equals 0 in the absence of crystallinity. Assuming that the peak ratio is proportional to the degree of crystallinity,\(^{[35]}\) it can be concluded that a linear fit of the peak ratio \(h_{998}/h_{973}\) can be used to describe the enthalpy of fusion if it is determined correctly

\[ \Delta H_m = k \times \frac{h_{998}}{h_{973}} \]  

(8)

If the data points deviate significantly from the straight line, the correct determination of the enthalpy of fusion would be questionable. Figure 6a shows that the linear fit using
Equation (8) describes both datasets well. It becomes clear that both evaluation methods show comparable agreement with the fit, whereas the method of added and subtracted enthalpies shows slightly better coefficients of determinations. This result supports the hypothesis that both recrystallization of amorphous parts of polypropylene and transformation from mesomorph to α-crystalline phase take place during heating. Furthermore, the determination of the peak ratio via FTIR enables the evaluation of the degree of crystallinity quickly and nondestructively (Figure 6b).

4. Conclusion

In this study, the enthalpy of fusion of polypropylene was determined by a systematic calibration method using the combination of DSC, XRD, and FTIR. The enthalpy of fusion of the α-crystalline i-PP (distributed under the trade name Moplen HP561R by LyondellBasell) was determined to be 170 ± 3 J g⁻¹. This value shows good correlation with a few of the studies published in the past decades (Figure 7). To the best of our knowledge, the enthalpy of fusion reported here is the most robust and consistent value published to date due to a broad range of crystallinities used for the calibration and an external validation procedure via FTIR. The determination of the enthalpy of fusion of polypropylene with other molar mass distributions or copolymers as well as completely different polymers using the method presented here may be the goal of future studies.

Acknowledgements

The authors would like to acknowledge Lisa Freund, Steffen Neumeier, and Professor Mathias Göken from the Department of Materials Science, Institute I: General Materials Properties from the University of Erlangen-Nuremberg (FAU) for the possibility to carry out the XRD measurements and for their guidance throughout the experiments. Thanks are due to Dr. Judith Roether for revising the manuscript.

Conflict of Interest

The authors declare no conflict of interest.

Keywords
differential scanning calorimetry, Fourier-transform infrared spectroscopy, heat of fusion, polypropylenes, X-ray diffraction

References

[1] D. Mileva, M. Gahleitner, D. Gloger, D. Tranchida, *Polym. Bull.* 2018, 831, 501.
[2] D. G. M. Wright, R. Dunk, D. Bouvart, M. Autran, *Polymer* 1988, 29, 793.
[3] A. van der Wal, J. J. Mulder, R. J. Gaymans, *Polymer* 1998, 39, 5477.
[4] G. W. Ehrenstein, P. Trawiel, G. Riedel, *Thermal Analysis of Plastics: Theory and Practice*, Hanser Verlag, München 2004.
[5] J. G. Fatou, *Eur. Polym. J.* 1971, 7, 1057.
[6] G.-y. Shi, B. Huang, J.-y. Zhang, *Makromol. Chem. Rapid Commun.* 1984, 5, 573.
[7] S. Haftka, K. Könnecke, *J. Macromol. Sci. B* 1991, 30, 319.
[8] J. X. Li, W. L. Cheung, D. Jia, *Polymer* 1999, 40, 1219.
[9] C. Minogianni, K. G. Gatos, C. Galiotis, *Appl. Spectrosc.* 2005, 59, 1141.
[10] A. S. Nielsen, D. N. Batchelder, R. Pyrz, *Polymer* 2002, 43, 2671.
[11] R. W. Wilkinson, M. Dole, *J. Polym. Sci.* 1962, 58, 1089.
[12] D. W. van Krevelen, *Makromol. Chem.* 1971, 132, 195.
[13] A. Kilic, K. Jones, E. Shim, B. Pourdeyhimi, *Macromol. Res.* 2016, 24, 25.
[14] J. A. Currie, E. M. Petruska, R. W. Tung, *Anal. Calorim.* 1974, 3, 569.
[15] D. W. van Krevelen, K. te Nijenhuis, *Properties of Polymers: Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions*, Elsevier, Amsterdam 2009.
[16] G. W. Ehrenstein, G. Riedel, P. Trawiel, *Thermal Analysis of Plastics*, Hanser Verlag, München 2004, p. 15.
[17] F. J. Lanyi, P. Kunzelmann, D. W. Schubert, *Macromol. Symp.* 2016, 365, 194.
[18] A. Kilic, K. Jones, E. Shim, B. Pourdeyhimi, *Macromol. Res.* 2016, 24, 25.
[19] A. Kilic, K. Jones, E. Shim, B. Pourdeyhimi, *Macromol. Chem.* 1975, 176, 1885.
[20] E. Passaglia, H. K. Kevorkian, *J. Appl. Phys.* 1963, 34, 90.
[21] W. W. Wilski, *Kunststoffe* 1960, 50, 335.
[22] G. W. Ehrenstein, G. Riedel, P. Trawiel, *Thermal Analysis of Plastics*, Hanser Verlag, München 2004, p. 15.
[23] A. Fichera, R. Zannetti, *Macromol. Chem.* 1975, 176, 1885.
[24] G. W. Ehrenstein, G. Riedel, P. Trawiel, *Thermal Analysis of Plastics*, Hanser Verlag, München 2004, p. 15.
[25] G. W. Ehrenstein, G. Riedel, P. Trawiel, *Thermal Analysis of Plastics*, Hanser Verlag, München 2004, p. 15.
[26] G. W. Ehrenstein, G. Riedel, P. Trawiel, *Thermal Analysis of Plastics*, Hanser Verlag, München 2004, p. 15.
[27] G. W. Ehrenstein, G. Riedel, P. Trawiel, *Thermal Analysis of Plastics*, Hanser Verlag, München 2004, p. 15.
[28] J. Zhao, Z. Wang, Y. Niu, B. S. Hsiao, S. Piccarolo, J. Phys. Chem. B 2012, 116, 147.
[29] W. Heinen, J. Polym. Sci. 1959, 38, 545.
[30] Y. Li, H. Liu, J. Song, O. J. Rojas, J. P. Hinestroza, ACS Appl. Mater. Interfaces 2011, 3, 2349.
[31] D. R. Burfield, P. S. T. Loi, J. Appl. Polym. Sci. 1988, 36, 279.
[32] G. Lamberti, V. Brucato, J. Polym. Sci. B Polym. Phys. 2003, 41, 998.
[33] H. Tadokoro, M. Kobayashi, M. Ukita, K. Yasufuku, S. Murahashi, T. Torii, J. Chem. Phys. 1965, 42, 1432.
[34] F. J. Lanyi, N. Wenzke, J. Kaschta, D. W. Schubert, Polym. Test. 2018, 71, 49.
[35] P. Böckh, T. Wetzel, Wärmeübertragung: Grundlagen und Praxis, Springer, Heidelberg 2014.
[36] J. Grebowicz, S.-F. Lau, B. Wunderlich, J. Polym. Sci. C: Polym. Symp. 1984, 71, 19.
[37] W. J. O’Kane, R. J. Young, A. J. Ryan, W. Bras, G. E. Derbyshire, G. R. Mant, Polymer 1994, 35, 1352.
[38] V. Caldas, G. R. Brown, R. S. Nohr, J. G. MacDonald, L. E. Raboin, Polymer 1994, 35, 899.
[39] K.-h. Nitta, K. Odaka, Polymer 2009, 50, 4080.