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Determination of the enthalpy of solid phase transition for isotactic polypropylene using a modified DSC technique

Jinan Cao *, Igor Sbarski

Faculty of Engineering and Industrial Sciences, Swinburne University of Technology, P.O. Box 218 Hawthorn, 533-545 Burwood Road, Hawthorn, Vic. 3122, Australia

Abstract

This paper investigates the enthalpy of solid phase transition of isotactic polypropylene from the mesomorphic phase to the monoclinic crystal form using DSC. iPP fibres with either monoclinic crystal form or mesomorphic phase were obtained by varying the conditions of melt spinning. XRD and mechanical tests were used to confirm the crystal forms. It is found that conventional DSC techniques fail to detect the transition enthalpy; a technique using silicon oil as the thermal medium was then employed to determine the transition enthalpy, which is of 3% the melting enthalpy for crystallites with monoclinic form, or 6.1 J/g on 100% crystallinity basis.
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Keywords: Polypropylene; Solid phase transition; Enthalpy

1. Introduction

As a major engineering polymer, isotactic polypropylene is one of the most studied polymers, its structure and properties are well known and documented. There are two major crystal modifications forming in melt spinning, depending on the overall cooling conditions. One is the monoclinic structure and the other has a mesomorphic phase. In most cases, the monoclinic crystal modification will be obtained via various processes. However, the mesomorphic phase can be observed when iPP undergoes an extra rapid cooling process. These two crystal forms have very different lattice structures, resulting in different optical and mechanical properties [1–6]. X-ray diffraction studies have demonstrated that the monoclinic form is thermally stable, but not the mesomorphic phase, which undergoes solid phase transition to the monoclinic form at high temperatures [1–6]. For iPP fibre samples, in situ XRD and thermoluminescence studies showed the transition occurs at temperatures higher than 100 °C [7,8].

Unlike the optical and mechanical properties, the thermal property of iPP is less well documented. In fact, significant

variation for the melting enthalpy of iPP ranging from 2.65 to 10.94 kJ/mol has been reported [9,10]. From an analysis of the heat capacity of iPP, Bu, Cheng and Wunderlich concluded a theoretical value of 8.7 ± 1.6 kJ/mol for 100% crystallised iPP [9]. Although it is logical to expect that the enthalpy associated with the solid phase transition be detected by means of thermal analysis, typically DSC, for many years DSC measurements have shown no measurable solid phase transition enthalpy. Indeed the DSC curves from our laboratory for the fibre with the mesomorphic phase appeared often very similar to those for the fibre with the monoclinic structure.

A recent paper by Androsch and Wunderlich reported iPP film with the mesomorphic phase by quenching. They showed X-ray diffraction pattern changes with heating showing the sample transferring into the monoclinic crystal form. They detected an exotherm thought to correspond to the crystal transition. However, no quantitative value was reported in their publications [11]. In addition, an endothermic event with its peak at 320 K considered somewhat above the glass transition temperature was observed on the DSC curve, indicating that there might be some how intrinsic difference between Androsch and Wunderlich samples and those we used for this study.

The aim of this study was to show how a modified DSC technique can be useful to determine the solid phase transition enthalpy, the enthalpy of solid phase transition is one of the most important fundamental thermodynamic properties.

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* Corresponding author. Tel.: +61 3 9214 8600; fax: +61 3 9214 5050.
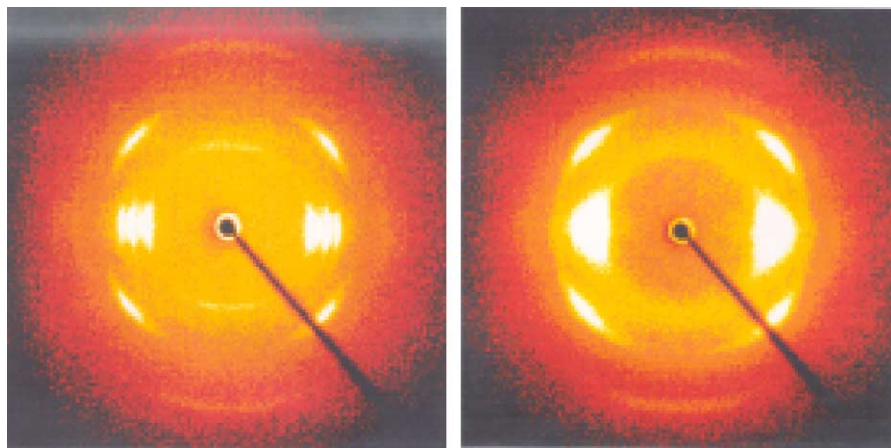*E-mail address:* jcao@swin.edu.au (J. Cao).

Fig. 1. X-ray diffraction patterns for the iPP fibres. (L) Monoclinic form; (R) mesomorphic phase.

2. Experimental

iPP fibre with the monoclinic phase was obtained though a melt spinning process under normal cooling conditions widely adopted, while iPP fibre with the mesomorphic phase was obtained under an extra rapid cooling condition. X-ray diffraction experiments were carried out using a nickel-filtered Cu Kα radiation source at $40 \, kV \times 30 \, mA$ with a general area detector system (GADDS, Siemens Germany) at a sample-detector distance of 50 mm to confirm the crystal structure of the fibres.

Mechanical testing for the iPP fibres with different crystal modifications was carried out on a Zwick 2010 tester with a fibre clamping accessory. A gage length of 20 mm was adopted for all the tests at a strain rate of 100%/min.

A TA Instrument 2920 was employed for DSC studies. The fibres were cut using scissors to fine fragments approximately 0.2–0.5 mm long. The fragmented fibres were packed into aluminium non-hermetic pans and sealed using the TA Instruments Sample Encapsulating Press. The DSC runs were carried out at 10 °C/min for heating and 5 °C/min for cooling. The nitrogen gas flow was 50 ml/min. Instrumental calibration was carried out using indium as the standard.

In order to use silicon oil as the thermal medium, hermitic aluminium pans were used to allow sealing of the oil inside pan. Around 5 mg accurately weighed fibre fragments were pressed into a disk using a stainless steel die, and placed into the pan. Five microlitre silicon oil was then injected into the pan with care not spilling outside. The pan was then sealed using the TA Instruments Sample Encapsulating Press for measurement. The main technical specifications of the silicon oil used as the thermal medium were high temperature stability, flush point 315 °C, density 1.050 g/cm^3, refractive index= 1.4950 (as described in the Aldrich Handbook of the fine chemicals and laboratory equipment).

3. Results and discussion

Displayed in Fig. 1 are the wide-angle X-ray diffraction (WAXD) patterns of the iPP fibres. The left one shows the monoclinic crystal form, with characteristic diffraction

spots of (110, 040 and 130) on the equator; the right hand side picture shows the diffraction pattern of the mesomorphic phase, which resulted from a relatively quick cooling spinning condition. From the diffraction patterns, it is understood that both samples have relatively high crystallinity as well as high molecular orientation.

These fibres have very different mechanical property as well. From the strain–stress curves obtained by tensile testing, the tensile modulus and elongation at break were obtained. These are shown in Table 1. The specimen with the monoclinic crystal modification showed superior performance as compared with the fibre with the mesomorphic phase. The tensile modulus is well in agreement with the reported 1380 MPa in the literature [12].

A raw DSC curve, as obtained from the measurement, for the iPP sample with the mesomorphic phase is displayed in Fig. 2. The sample was heated up to 185 °C detecting the melting endotherm, and cooled down to monitor re-crystallisation behaviour. The same DSC curve for the sample with the monoclinic crystal form is shown in Fig. 3. A melting endotherm with its peak at 162 °C on heating and a re-crystallisation exotherm with its peak at around 120 °C on cooling were detected, and the two values were consistent, indicating that molten crystallites were re-crystallised during cooling. However, there is no exotherm that can be considered to correspond to the solid phase transition from the mesomorphic phase to the monoclinic.

The experiments were repeatedly carried out, and the results were highly reproducible. This is unexpected because in situ XRD and thermoluminescence showed clear transition at above 100 °C [7,8,11].

This result is also different from the results reported in the literature. Androsch and Wunderlich reported an exotherm

Table 1
Main mechanical properties of the iPP fibres with different crystal forms

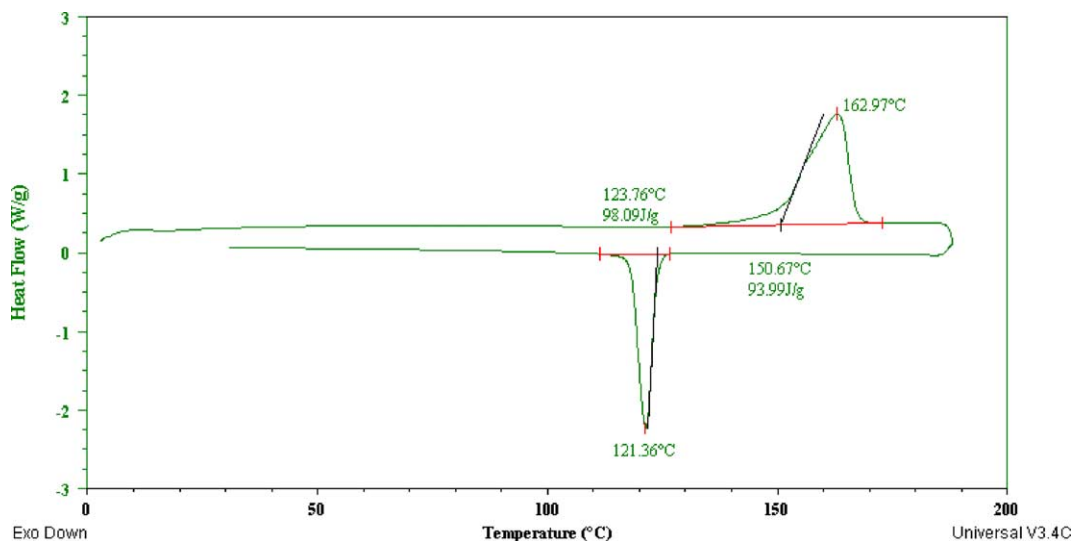| Property	Crystal form	
	Monoclinic	Mesomorphic
Tensile modulus (MPa)	1570	1120
Elongation to break (%)	257	203

Fig. 2. DSC heating and cooling curve for the iPP fibre with the mesomorphic phase, measured using non-hermitic pans. Melting and re-crystallisation are observed, but no exotherm corresponding to the solid phase transition can be identified.

thought to correspond to the phase transition at low temperature. However, no quantitative value was reported in their publications [11]. In addition, an endothermic event with its peak at 320 K considered somewhat above the glass transition temperature was observed on the DSC curve. On the other hand, Fichera and Zannetti's reported an exotherm starting from around 80 °C and as large as 16.7 J/g for quenched iPP. For the quenched and annealed iPP, a further endotherm appeared. It is thus reasonable to consider that there might be some how intrinsic difference between Androsch and Wunderlich's and Fichera and Zannettis samples and those we used for this study.

There is no doubt that the transition enthalpy is small. Careful analysis of the DSC result indicates that this may be a result of poor thermal transfer for the fibre samples, which may curl while the temperature rises, indicating that measurements using modified DSC techniques are desirable before

concluding there is no detectable enthalpy difference between the two crystal forms for iPP.

The iPP samples were packed into hermitic aluminium DSC pans with 5 μl silicon oil as the thermal medium. Silicon oil provides faultless thermal contact with the DSC pans, and maintains constant thermal transfer even while the fibre samples are curling as a result of temperature rises. This DSC technique has demonstrated its usefulness for studies of biological keratin materials [13–16]. The result DSC curves are shown in Figs. 4 and 5. For the fibre with the mesomorphic phase, besides the melting endotherm at high temperature 164 °C, there is a small broad exotherm identifiable in between 103 and 135 °C with its peak at 125 °C. This exotherm is considered to correspond to the solid phase transition from the mesomorphic phase to the monoclinic crystal form, which is followed by an endotherm that results from melting of crystallites with the monoclinic crystal form. It is thus
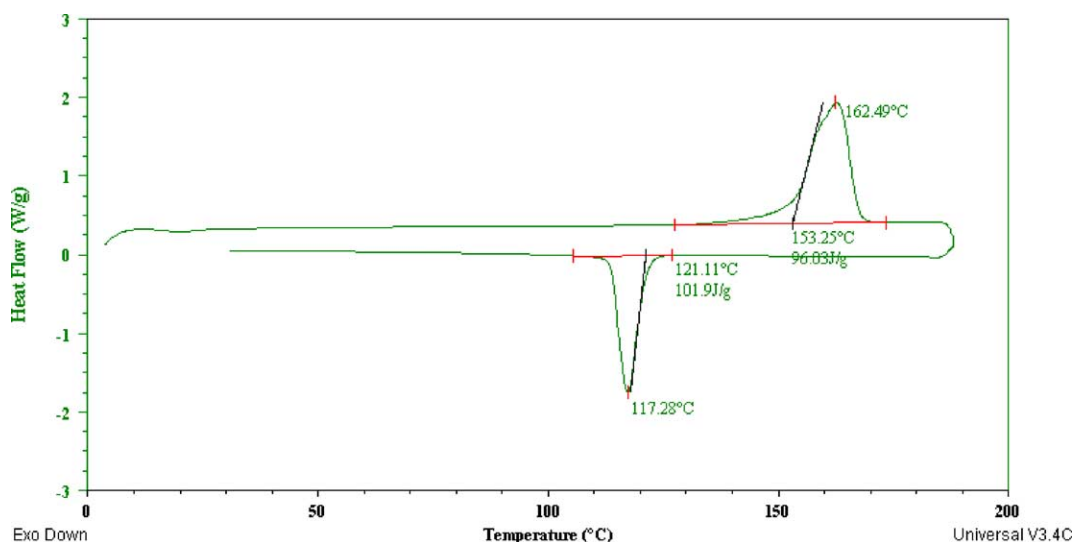

Fig. 3. DSC heating and cooling curve for the iPP fibre with the monoclinic crystal modification, measured using non-hermitic pans. Melting and re-crystallisation are observed.
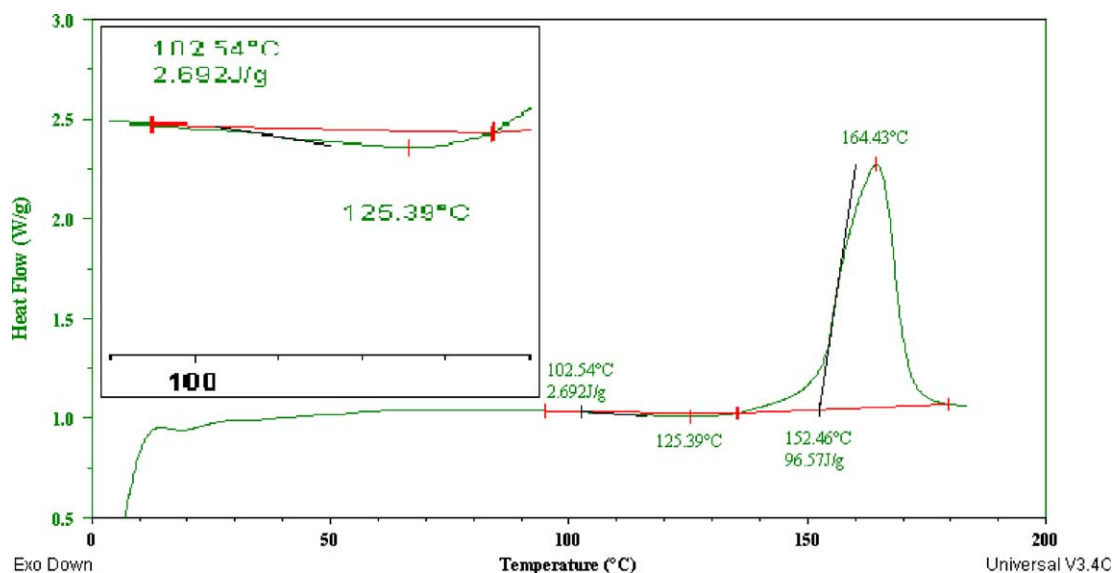
Fig. 4. DSC heating curve for the iPP fibre with the mesomorphic phase, measured using hermitic pans with silicon oil as the thermal medium. In addition to the melting endotherm, a small exotherm corresponding to the solid phase transition is identified.
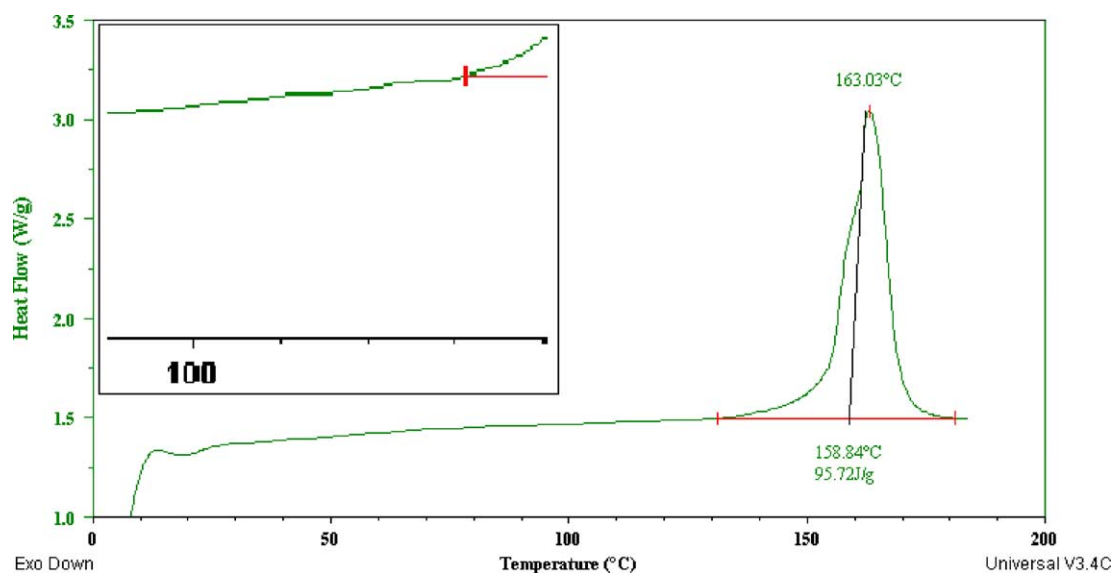

Fig. 5. DSC heating curve for the iPP fibre with the monoclinic crystal modification, measured using hermitic pans with silicon oil as the thermal medium.

confirmed that the mesomorphic phase undergoes solid phase transition into the monoclinic from above 100 °C, then melt as the crystallites with the monoclinic modification. Improved thermal transfer by silicon oil resulted in a higher sensitivity required to detect the solid phase transition enthalpy. This modified technique was also used to compare the DSC curve for the iPP sample with the monoclinic crystal form; as expected, no transition exotherm can be observed in Fig. 5, which shows the DSC curve for the iPP fibre with the monoclinic crystal form. The DSC curve is flat until the endotherm ranging from 132 to 173 °C with its peak at 163 °C for crystallites melting. It should be mentioned that all these DSC experiments were highly reproducible. To highlight these features, enlarged curves are inserted in Figs. 4 and 5.

The transition enthalpy of 2.8 J/g for the iPP sample with the mesomorphic phase was obtained by averaging five runs. On the other hand, the major melting enthalpy was obtained 95.4 J/g. The transition enthalpy is about 3% of the melting enthalpy. Using the theoretical melting enthalpy of 8.7 ± 1.6 kJ/mol (206.7 ± 38.02 J/g: PP unit molecular weight 42.0804) as a standard, one obtains the degree of crystallinity 46% for the iPP fibres. The enthalpy for the solid phase transition from the mesomorphic phase to the monoclinic is thus calculated 6.1 J/g on 100% crystallinity basis.

Acknowledgements

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