

ADIABATIC CALORIMETRY OF A VERY LOW DENSITY POLYETHYLENE COPOLYMER

J. C. van Miltenburg¹, V. B. F. Mathot², P. J. van Ekeren¹ and L. D. Ionescu³

¹Chemical Thermodynamics Group, Padualaan 8, 3584 CH Utrecht

²DSM, Research, P.O. Box 18, 6160 MD Geleen, The Netherlands

³Faculty of Chemistry, Al. I. Cuza University of Iasi, P.O. Box 10-2022, 6600-Iasi, Romania

Abstract

The heat capacity of a very low-density polyethylene copolymer (VLDPE) was measured between 10 and 410 K. Using two sets of literature data for the fully crystalline and the fully amorphous states, crystallinities were calculated as a function of temperature. During the stabilisation periods in the melting process no equilibrium is reached, because of an exothermic process, which is attributed to (re)crystallization. Values for the enthalpy of melting and for the heat capacity of the liquid are given.

Keywords: calorimetry, crystallinity, polyethylene

Introduction

Adiabatic calorimetry allows a precise determination of the heat capacity over a large temperature region and, due to its intermitted character, gives also information about the stability of the polymer under investigation. For polymers, heat capacity, enthalpy and derived quantities like crystallinity are important quantities to determine by thermal methods [1–3]. In this communication, such results are reported for an ethylene-1-octene VLDPE, which copolymer shows very broad crystallisation and melting regions [4, 5]. The assumption, needed for the crystallinity determination, that the material consists of crystalline and amorphous parts and that its thermodynamic properties may be calculated as the sum of the properties of the constituent parts, is known to hold for this copolymer [4].

Experimental

The ethylene-1-octene VLDPE has a 1-octene content of 6.2 mol%. Its M_w is 95 kg mol⁻¹ and the density after compression molding is 902 kg m⁻³.

The calorimeter, laboratory design indication CAL V [6], was described before. The thermometer, a 27-ohm Rhodium-Iron resistance, was calibrated by Oxford Instruments at 33 points between 1.5 and 300 K. The calibration was extended to 420 K using the melting temperatures of naphthalene and indium. Conversion to the ITS-90 scale was based on the article of Goldberg and Weir [7]. A sample of 6.166 g

was enclosed in the calorimeter. After evacuation, about 1000 Pa of helium was admitted in order to enhance the heat transfer in the vessel. Measurements were made in the intermittent mode, stabilization periods were followed by input periods under automatic control. During the whole measurement, a second computer regulated the shields and the wire heater to within 0.002 K of their set point. A total of 11 series were measured. The thermal history of the sample proved to be important for the detailed appearance of the melting process. Before cooling from the melt the sample was held at about 410 K for at least one hour. In short, the experiments can be divided into three groups;

- Melting of the product as received, thus after a prolonged storage time at room temperature. This is series 1.
- Measuring of the sample after crystallisation from the liquid at a 'normal' cooling rate, being about 4 K min⁻¹. These experiments include the series 2 till 9.
- Measuring after equilibration in the melt at 396.3 K for two hours and subsequent very slow cooling, at a rate of 1 K h⁻¹. These results are to be found in the series 10 and 11.

The calculation outside the transition regions was performed in the usual way by extrapolation of the for- and after period to the mid-point of the input period. In the transition region, comprising the glass transition and the melting region, which together span the range between 200 and 405 K, this method of calculation was not applicable. Waiting for thermal equilibrium would ask for stabilization periods of 10 000 s or more and apart from being unpractical, it would increase the errors in the heat capacity determination due to extrapolation. Using the known heat transfer to the surroundings (from an empty vessel experiment) together with the applied electrical energy we calculated the enthalpy increment between the midpoints of the stabilization periods. This method is very precise as the heat transfer is only in the order of 0.1% of the electrical input. In this way the actual enthalpy path followed by the vessel and its contents is measured. The observed temperature drifts in the stabilization periods do give additional information about the process at hand, much like the information obtained in temperature modulated DSC.

Results

In Fig. 1 the heat capacity of the sample is given between 10 and 410 K. This Fig. combines series 4 till 8. Data of the series 2, 3 and 9, made under comparable conditions coincide almost completely with the curve given in this plot and are omitted for clarity. The main aspect of this curve is the glass transition region around 230 K, followed almost immediately by the start of the melting process. A broad low melting peak and a high melting peak are seen, reflecting the highly and the hardly branched chains in the ethylene-1-octene copolymer [4, 5] respectively. In Fig. 2 examples of the three sorts of melting experiments are given: series 1, melting of a sample previously stored at room temperature; series 3, melting of a sample cooled at 4 K min⁻¹; and series 11, an extremely slowly cooled sample. In series 1 the storage at room temperature is reflected by a hump in the curve around 310 K. Series 3 shows a more

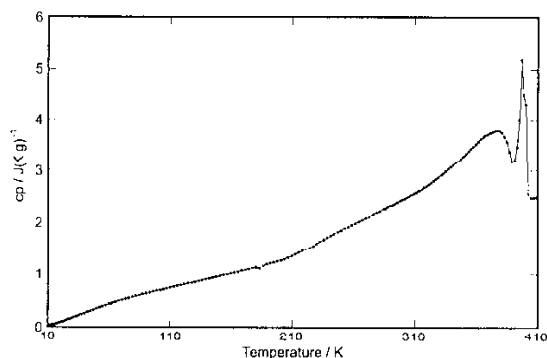


Fig. 1 Experimental heat capacity data. Series 4 till 8

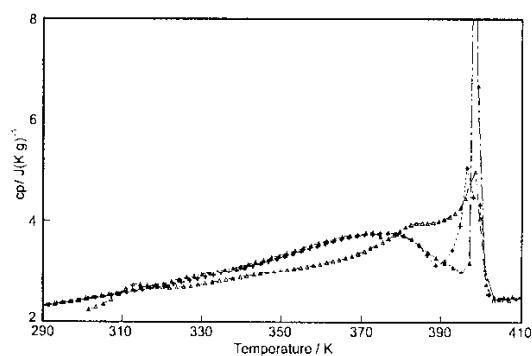


Fig. 2 Three melting experiments with different thermal history. Δ – Series 1 measurement of sample as received, thus after a long storage time. $+$ – Series 3, immediately after melting and cooling at a rate of 4 K min^{-1} , \blacktriangle – Series 11, after cooling at a rate of 1 K h^{-1}

smooth melting behavior, with the high melting peak having a shoulder which is caused by recrystallization. Slow cooling (series 11) dramatically changes the shape of the highest melting peak, reflecting stable crystallites not capable of recrystallization.

Calculation and discussion

Besides the experimentally determined c_p -data (c_p) of the series 4 till 6, the tabulated values for the fully crystalline (c_{pc}) and fully amorphous phase (c_{pa}) of linear polyethylene as given by Varma-Nair and Wunderlich [2] and Mathot [3] were used. Based on these data the crystallinities were calculated – assuming no excess phenomena – between 10 and 200 K using

$$w_c(T) = \frac{c_{pa}(T) - c_p(T)}{c_{pa}(T) - c_{pc}(T)}$$

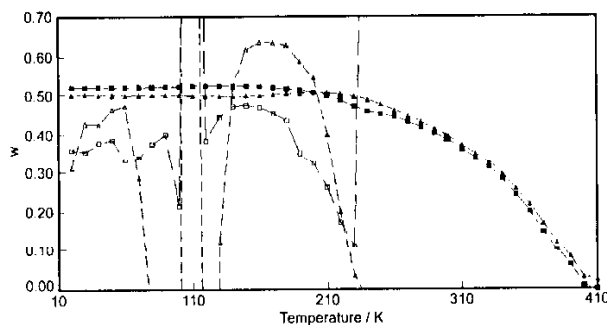


Fig. 3 Calculated crystallinity as a function of temperature. The solid symbols refer to the calculation based on the enthalpy, the open symbols to the calculation based on the heat capacity. \square – was calculated using the ATHAS databank [2], Δ – using reference [1]

The differences in the c_p -values are quite small, thus giving raise to large deviations in the w^c -calculation. Around 100 K the reference values for the crystalline and amorphous states almost coincide and this way of calculating w^c is no longer meaningful. The crystallinity can also be calculated in an analogous way using the enthalpy data. These results are much smoother, in Fig. 3 the results of both ways of calculating w^c are given. The two literature data sets do give a slightly different result (in the order of 3%) between 10 and 200 K, above this temperature they almost coincide. In Fig. 4 the measured heat capacities together with the literature values for both phases are given between 100 and 300 K. Assuming a crystallinity of 0.5 (Fig. 3), the curves for 50% crystalline and 50% amorphous and for 50% crystalline and 50% liquid were calculated. The liquid values were extrapolated from our measurements (as if there is no glass transition), the other values from the tables of Wunderlich [2] (in which case a glass transition around 237 K is included). As can be seen from this Figure melting starts in the glass transition range. At the glass transition, the temperature of the inflexion point in the heat capacity curve was estimated to be 230 K. As is known, the glass transition temperature depends on various parameters, amongst with comonomer type and amount.

The crystallization process

In the slow cooling experiment, preceding series 11, the sample was first heated till 396.3 K (just before the end of the melting process). It was stabilized at this temperature for two hours. Then the setting of the shields was adjusted to give a cooling rate of 1 K h^{-1} . Cooling was interrupted at 375 K and the temperature was followed for a few hours. Crystallization continued on a small scale for a long time with an estimated time constant of about two hours.

The melting process

The enthalpy of fusion was calculated using as the start of the base line the curve for 50% crystalline and 50% liquid material (Fig. 4). An iterative method was ap-

plied, in which the melted fraction was calculated and used to recalculate the base line.

Series	Melting enthalpy/J g ⁻¹	Remark
s 2+s 3	251	quickly cooled (4 K min ⁻¹)
s 8+s 9	258	longer stabilization times
s 10+s 11	259.2	cooled at 1 K h ⁻¹

These values do depend on the thermal history, they are somewhat lower than the value of 276.5 J g⁻¹ or 3.979 kJ mol⁻¹ for polyethylene (molar mass 14.04) adopted in the NIST Chemistry Webbook (<http://webbook.nist.gov/chemistry>).

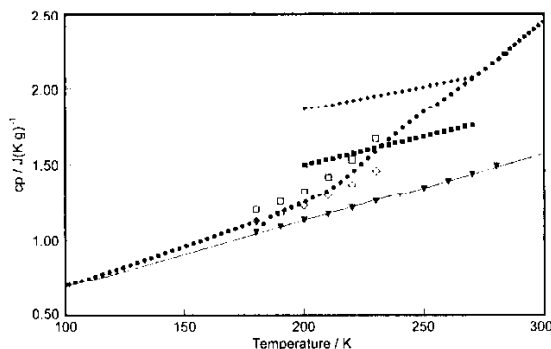


Fig. 4 Experimental heat capacities in the vicinity of the glass transition. The literature data for the completely crystalline and completely amorphous phase are given together with the calculated curves for 50% crystallinity. ● – Experimental data; ▼ – Crystalline values; ◆ – 50% crystalline + 50% amorphous; ◻ – amorphous phase; ◆ – extrapolated liquid phase

During the melting process the temperature drifts in the stabilization periods were recorded. At low temperatures, below 320 K, the drift was slightly negative (meaning an endothermic process), above this temperature it became more and more positive (meaning an exothermic process). In Fig. 5 the heat capacities in the melting region of series 3 are given together with the observed temperature drifts. It is clear that the temperature drift curve has the same shape as the heat capacity curve. The same behavior was observed in the series 1 and 8. The interpretation of the exothermic drift is (re)crystallization during the stabilization periods during heating, as has been measured using TMDSC and which is now verified in an unequivocal way. A very intriguing aspect, however, is the fact that drift occurs all the way to the end of melting. In series 11, after the slow cooling, the exothermic effect is much smaller – as expected – and the drift becomes negative around 398 K.

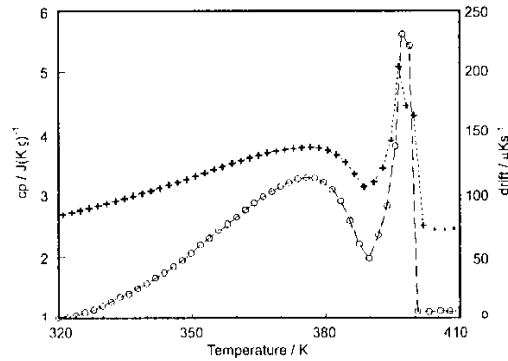


Fig. 5 Heat capacity and thermal drift in the melting region. + – heat capacity data; o – drift of the vessel in $\mu\text{K s}^{-1}$ (right axis)

The liquid phase

In Fig. 6 collected heat capacity data of the liquid are given. All series show significant lower values as compared to the literature data [1, 2]. A fit of the last series (series 11) resulted in

$$c_p / \text{J K}^{-1} \text{g}^{-1} = 1.366 + 0.002769(T/\text{K})$$

These values are about $0.04 \text{ J K}^{-1} \text{g}^{-1}$ lower than the values given by Wunderlich and Mathot [1, 2]. Remarkably, the first series show a progressive increase in heat capacity. In the subsequent series the heat capacity of the liquid immediately after melting starts with the value with which the previous series ended. This phenomenon ended at the series 11. So, possibly, the heat capacity increase depends on the time spent in the liquid phase.

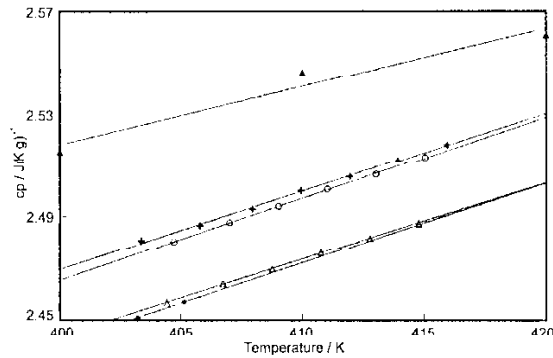


Fig. 6 Heat capacity of the liquid phase. • – Series 1; Δ – series 3; o – series 8; + – series 11. The literature data are given by \blacktriangle

Conclusions

It has been shown that adiabatic calorimetry gives valuable information on heat capacity, enthalpy, crystallinity of the copolymer studied. As for the exothermic effects during the melt and the increase in heat capacity of the liquid with time, more information will be needed to come to a complete explanation.

References

- 1 V. B. F. Mathot, *Calorimetry and Thermal Analyses of Polymers*, Hanser, Munich, 1994.
- 2 M. Varma-Nair and B. Wunderlich, *J. Phys. Chem. Ref. Data*, 20 (1991) 349.
- 3 V. B. F. Mathot, *Polymer*, 25 (1984) 579.
- 4 V. B. F. Mathot and M. F. J. Pijpers, *J. Appl. Polymer Science*, 39 (1990) 979.
- 5 R. A. C. Deblieck, and V. B. F. Mathot, *J. Material Science Letters*, 7 (1988) 1276.
- 6 J. C. van Miltenburg, G. J. K. van den Berg and M. J. van Bommel, *J. Chem. Thermodyn.*, 19 (1987) 1129.
- 7 R. N. Goldberg and R. D. Weir, *Pure and Appl. Chem.*, 64 (1992) 1545.