Influence of different types of differential scanning calorimeter on analyses of polyphenylacetylene

A.S. Luyt[a],*, H.C.M. Vosloo[b]

[a] *Department of Chemistry, University of the North (Qwaqwa Campus), Private Bag X13, Phuthaditjhaba, 9866, South Africa*
[b] *Department of Chemistry, Potchefstroom University for Christian Higher Education, Potchefstroom, 2520, South Africa*

Abstract

Polyphenylacetylene (PPA), synthesized by metathesis polymerization of phenylacetylene in the presence of a $Mo(CO)_6$–C_6H_5OH catalytic system at 120°C, was analysed using two different differential scanning calorimeters. Important discrepancies were observed between the results obtained on the two instruments; they are discussed in this note.

Keywords: Differential scanning calorimetry; Polyphenylacetylene (PPA)

1. Introduction

Polyphenylacetylene (PPA) samples, synthesized by metathesis polymerization of phenylacetylene in the presence of a $Mo(CO)_6$–C_6H_5OH catalytic system at 120°C, has previously been investigated thermo-analytically [1,2]. All the DSC results reported were obtained on TA Instruments DSC 910S. When the work was repeated on Perkin–Elmer DSC 7, we found little agreement between the curves obtained on the two instruments. The differences between the two instruments are well known to the thermal analyst, the most important being that the Perkin–Elmer instrument is based on the power-compensation principle and that of TA Instruments on the heat-flux principle.

The differences between the DSC curves obtained on these two instruments and the problems experienced as a result of these differences, will be discussed in this communication.

---

* Corresponding author. Tel.: 058 713 0211 Ext. 1161; Fax: 058 713 0226.

2. Experimental

On both instruments DSC analyses were performed on 5–7 mg powder samples at a heating rate of $20°C$ min^{-1} and a nitrogen flow rate of 20 cm^3 min^{-1}. Open aluminium pans were used, but for comparison purposes hermetically sealed pans were also used in the Perkin–Elmer instrument.

3. Results and discussion

Figs. 1 and 2 compare the DSC curves of the same sample analysed in open pans on the two instruments. Two main differences are observed, namely (i) the peak shoulder at about $220°C$ is more clearly defined on the TA Instruments curve and (ii) an endotherm is observed at $350°C$ on the TA Instruments curve, which goes over into a second clearly defined exotherm.

The first endotherm, starting at about $50°C$ and observed on both curves, was characterized as the evaporation of chlorobenzene solvent from the polymer matrix [1]. The peak shoulder at about $220°C$, described as the onset of crystallization and/or solid state transition, is part of a much stronger exotherm which is accompanied by a considerable mass loss. This thermal event was identified as the onset of cross-linking and/or decomposition [1]. The second endotherm on the TA Instruments curve was found to correspond to the volatilization of 5'-phenyl-*m*-terphenyl together with small amounts of quaterphenyl, as identified through TG–MS analyses. These were the expected products from the decomposition mechanism proposed by us [1].
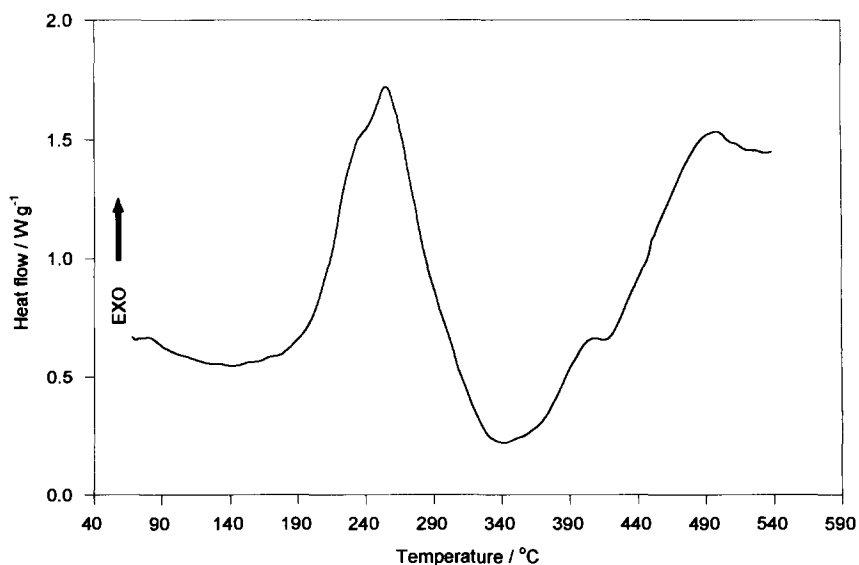

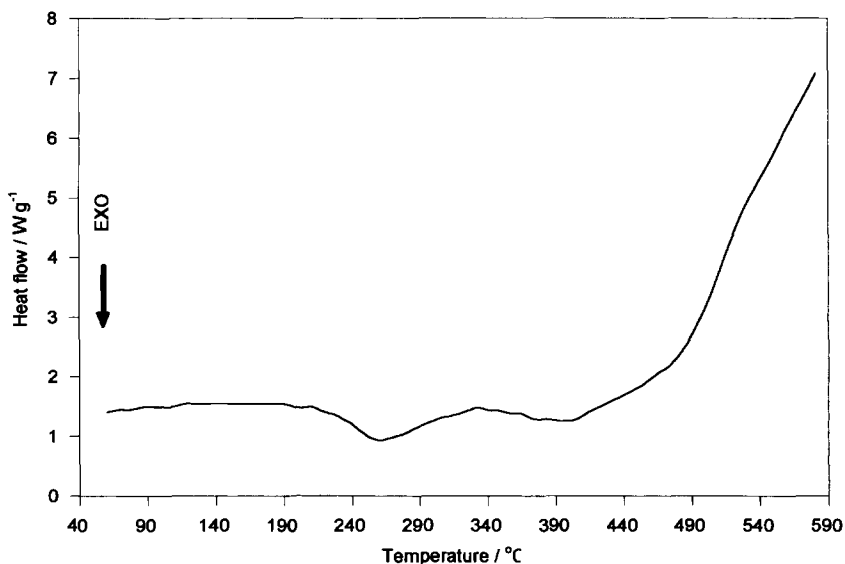Fig. 1. DSC heating curve of PPA in nitrogen (TA Instruments DSC 910 with open pan).

Fig. 2. DSC heating curve of PPA in nitrogen (Perkin–Elmer DSC 7 with open pan).

It was at this point that no correlation could be found between the curves obtained on the two instruments. On the Perkin–Elmer curve the last endotherm (clearly defined on the TA Instruments DSC curve) was only occasionally, and in Fig. 2 only weakly, observed followed by the DSC curve continuously progressing in an exothermic
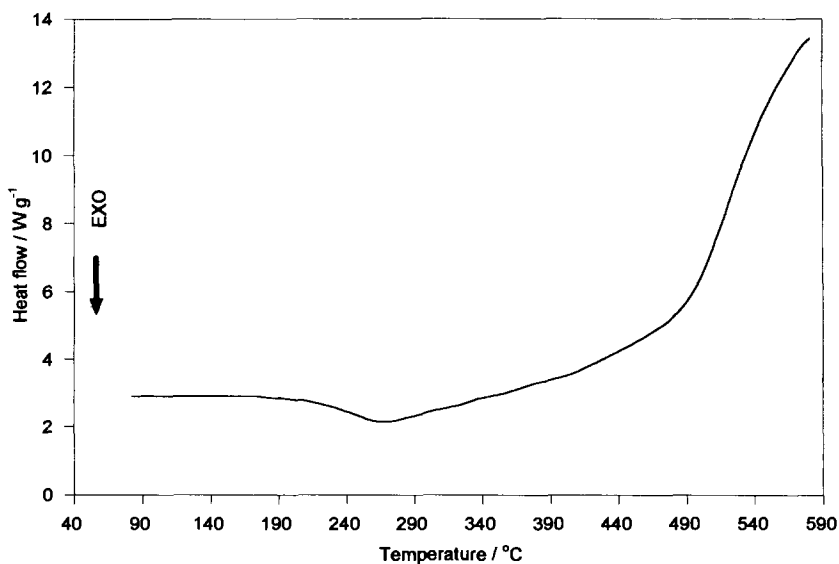

Fig. 3. DSC heating curve of PPA in nitrogen (Perkin–Elmer DSC 7 with hermetically sealed pan).

direction until the maximum analysis temperature was reached. Because decomposition and evaporation are the main thermal events at temperatures higher than 250°C, the difference between the two curves should have something to do with a particular instrument's sensitivity to the condition of sample holders, which is affected by the evolution of condensable matter. This may also have something to do with the way purge gas enters and exits the respective cells.

Apparently the Perkin–Elmer instrument is extremely sensitive to the evolution of condensable matter and, from the difference in construction of the two cells under discussion, one may accept that differences in the way purge gas enters and exits these cells also play a role in the problem we have in trying to compare the curves obtained on the two instruments. The above discussion also explains the less clearly defined peak shoulder at about 220°C, because decomposition and evaporation starts before the crystallization and /or solid state transition is finished and the Perkin–Elmer immediately senses the evolution of condensable matter and starts registering the latter.

In order to try and restrict the evaporation process in the Perkin–Elmer instrument, a hermetically sealed pan was used (Fig. 3). From this curve it is clear that there is no improvement.

4. Conclusion

It seems that, with our particular system, it is not possible to try and compare 'apples with apples' because of the large difference in the way the two instruments sense and register the strong evolution of condensable matter at temperatures above 250°C.

References

[1] H.C.M. Vosloo and A.S. Luyt, J. Therm. Anal., 44 (1995) 1261.
[2] A.S. Luyt and H.C.M. Vosloo, J. Therm. Anal., 44 (1995) 1277.