

A NEW STATE OF AGGREGATION?

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The DSC curve of succinonitrile shows a melting peak at approximately 60°C with the very small heat of fusion of 47 J/g. Further investigations in the low temperature range result in an additional exotherm at -60°C. On heating there are the two corresponding endotherms repeatedly.

We postulate a so called plastic crystalline mesophase between the two thermal effects.

Keywords: plastic crystalline mesophase, state of aggregation

Introduction

Recently we have been investigating potential temperature calibration materials melting in the proximity of 50°C. One of the substances studied was succinonitrile with a specified melting point of 54°C. The measured heat of fusion by DSC is only 45 J/g, which is three times less than the typical value of 150 J/g for organic substances. In addition the fusion peak is slightly odd shaped (Fig. 1). These curious facts require an explanation.

Is it due to some amorphous phase in the solid substance, which would also explain the tackiness of the compound? A DSC cooling curve in such a case often gives an exothermal peak of further crystallization. On reheating the melting peak should amount to approximately 150 J/g.

Experimental

The necessary measurements are performed in a Mettler TA4000 System with its DSC30 low temperature cell. The three diagrams in this paper are automatically measured by means of 3 linked temperature programs.

The succinonitrile is obtained from Fluka, Buchs, Switzerland (Order No. 14180).

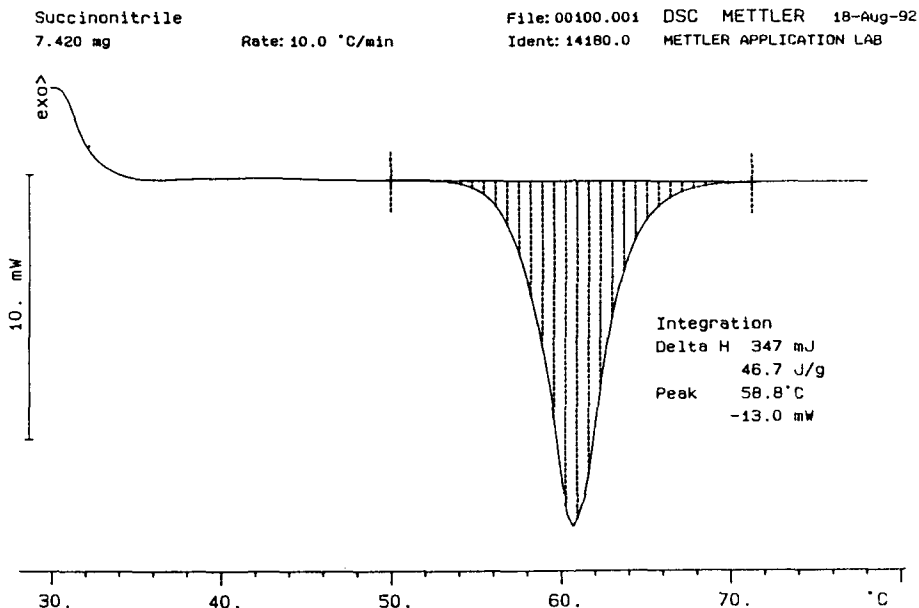


Fig. 1 DSC curve in the region of the 'official' melting point of succinonitrile. Compared with usual melting peaks the tail after the top of the peak is quite broad and the heat of fusion is very small

Results

Figure 2 clearly shows two sharp exothermal peaks over an interval of 100°C. The sum of the two heats of crystallization is 123 J/g. To prove complete crystallization the consecutive heating curve should exhibit one fusion peak of approximately 120 J/g in the area of +60°C. But succinonitrile is different: on reheating there are two fusion peaks, one at -35°C, the other at 60°C (Fig. 3). The heating and the cooling curves are completely repeatable. Since the substance is of plastic consistency between the peaks we postulate a plastic crystalline mesophase. This is in analogy to the liquid crystals.

Conclusion

Even simple substances of low molar mass can exhibit a surprising thermal behaviour. There is a lot of scientific work to be done for the investigation of the known million organic substances!

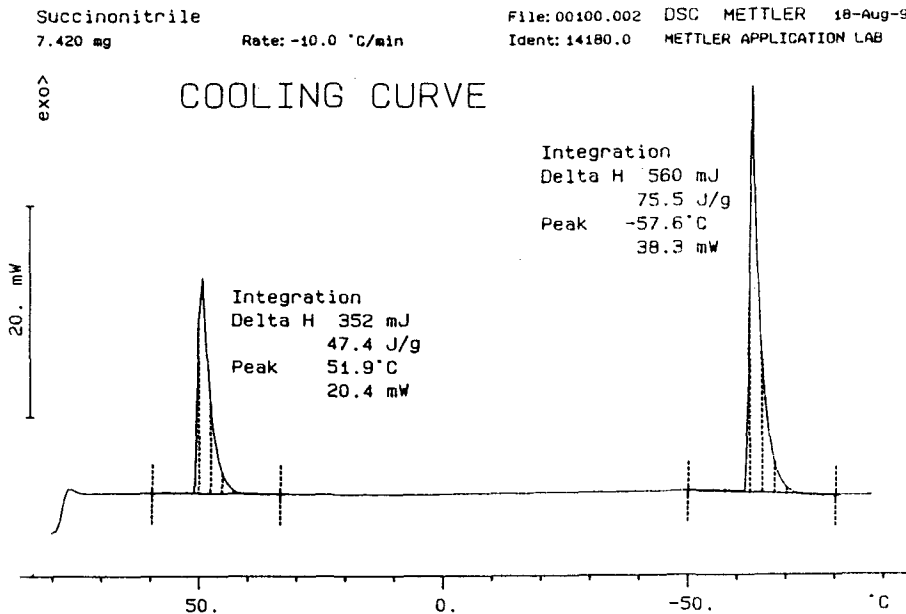


Fig. 2 The DSC cooling curve is measured with 10 deg.min⁻¹ after the heating curve (Fig. 1)

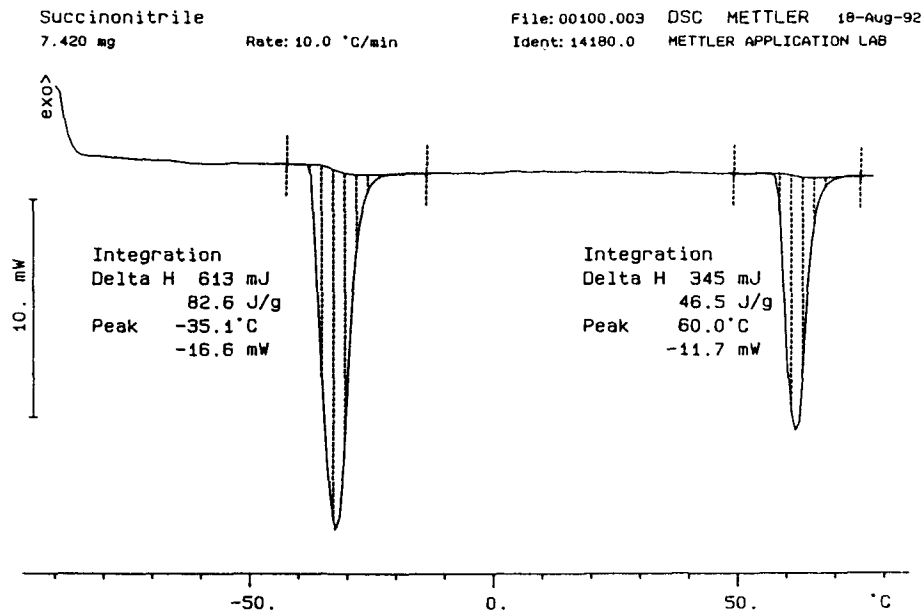


Fig. 3 This heating curve measured after cooling (Fig. 2) shows 2 'fusion peaks'

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During the poster session Dr. A. McGhie, University of Pennsylvania, Philadelphia confirmed our observation [1].

References

- 1 G. W. Smith, Plastic Crystals, (Ed. G. A. Brown), Advances in Liquid Crystals, Vol. 1, Academic Press, 1975.

Zusammenfassung — Die DSC-Kurve von Bernsteinsäurenitril zeigt bei etwa 60°C einen Schmelzpeak mit einer sehr geringen Schmelzwärme von 47 J/g. Weitere Untersuchungen im Tieftemperaturbereich zeigen einen zusätzlichen exothermen Peak bei -60°C. Beim Erhitzen sind die zwei entsprechenden endothermen Erscheinungen wiederholbar.

Zwischen den zwei thermischen Effekten postulieren wir eine sogenannte plastische kristalline Mesophase.