Journal of Thermal Analysis, Vol. 30 (1985) 1273—1281

APPLICATION OF SIMULTANEOUS THERMOMICROSCOPY/DSC TO THE STUDY OF PHASE DIAGRAMS

H. G. Wiedemann and *G. Bayer**

METTLER INSTRUMENTS AG, CH-8606 GREIFENSEE* INSTITUT FÜR KRISTALLOGRAPHIE UND PETROGRAPHIE DER ETH ZÜRICH, CH-8092 ZÜRICH, SWITZERLAND

The correlation between morphological changes and DSC recordings gives valuable information on the mechanism of phase transformations. The present paper describes a new instrument for simultaneous DSC and thermomicroscopy in transmitted light, where a DSC device is placed in a commercially available hot-stage. The application of this DSC/thermomicroscopy is exemplified by study of the phase diagrams for KNO_3—$NaNO_3$, diphenylamine—benzophenone and a liquid crystal system.

Results obtained from thermoanalytical measurements such as DSC are usually reproducible and quantitative, but they cannot always readily be correlated with the respective phase transformation or chemical reaction occurring in the substance. Attempts have therefore been made to improve such thermoanalytical methods by a correlation between their results and the physical or chemical changes of the substances investigated.

These combinations of methods have proved very successful. When performed simultaneously with DTA or DSC, for example, TG is a very powerful tool for studying the chemical stability and decomposition of a variety of materials. This paper demonstrates the usefulness of simultaneous DSC and hot-stage microscopy. Effects which do not show any significant enthalpy change in DSC can often be detected with microscopy. On the other hand, thermomicroscopic investigations often require estimates of heats of transformation, fusion or crystallization.

Further, thermomicroscopy with DSC is a very good teaching method to introduce beginners to thermoanalytical investigations, for one can see changes in the investigated substance together with the course of the measured curve. However, the method can also be used for theoretical and practical considerations. For example, differences in the measurement of the same substance in various crucible materials, e.g. glass, aluminium and sapphire, become visible and can be studied.

For the recognition of phase boundaries, it is mostly more simple if simultaneous thermomicroscopy/DSC can be used for the determination of phase diagrams, especially for very small concentrations of one of the components.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Instrumental

The simultaneous measurements are based on a commercial microscope and the hot-stage of the Mettler FP800 Thermosystem. The schematic (see Fig. 1) shows the microscope with the hot-stage and the FP800 control unit, which can be connected with a RS 232C to a personal computer system, wherein the evaluation programs are

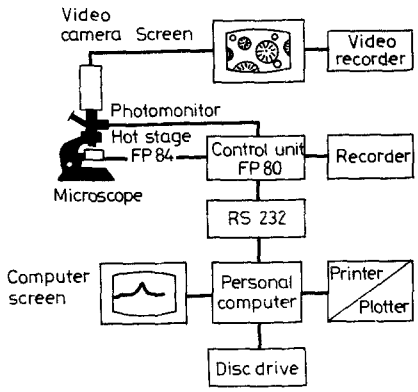

Fig. 1 Instrumental set-up for simultaneous hot stage microscopy

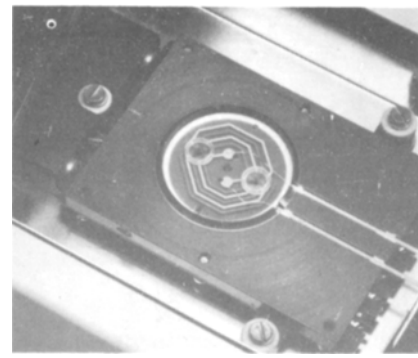

Fig. 2 Opened furnace of the hot stage with thermopile and sapphire crucibles

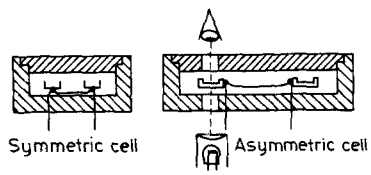

Fig. 3 Differences between conventional and microscopic DSC

accessible. In Fig. 2 part of the opened flat-bed furnace can be seen, containing the thermopile and the sapphire crucibles. The sample is filled directly into the crucible. In the case of low-viscosity substances and liquid crystals, three sapphire balls act as spacers and help to maintain a uniform sample distribution and thickness during the measurement.

The melting and transformation behavior of a substance depends, among others, on the size and shape of the crystals, and therefore microscopic observation is important to obtain reproducible results.

For stable experimental conditions, the illumination of the sample during the experiment needs a stabilized poly- or monochromatic light source. The illumination acts as an additional heating source and therefore causes asymmetric heat distribution in the cell (Fig. 3). This may be corrected by subtracting a blank from the measured curve.

Table 1 Instrumentation for thermomicroscopic analysis

		Microscope	
Oculars	Objectives	Filters	Light sources
		Simultaneously used accessories	
Hot stage	DSC-cell	Photometer	IR-spectrometer
		Sample holders	
Slides	Crucibles		Slide and crucible material
		Furnaces	
Temperature ranges		Heating programs	Atmospheres
		Optical recordings	
Cameras & film materials		TV cameras	Accessory items
		Computer evaluation of thermal measurements	
Computers	Interfaces	Hardware	Software

Table 2 Applications of thermomicroscopic analysis with and without DSC

Methods	Materials
Measurement of DSC-Curves	Investigation on Building Materials
Peak Integration	Thermal Stresses in Glasses
Purity Determination	Safety Explosives
Cp—Measurements	Alcohols and Fatty Acids
Morphological Studies	Decomposition of Edible Fats
Nucleation Phenomena	Fats, Waxes and Soaps
Kinetics of Crystal Growth	
Melting & Freezing Phenomena	Sugars, Starches & Pectins
Structural Transformations	Degradation Products of Wood
Glass Transitions	Pharmaceutical Purity Determination
Evaluation of Phase Diagrams	Thermal Stability of Emulsions
Dehydration Studies	Crystallization of Polymers
Isomerization of Organic Compounds	Transitions in Liquid Crystals
Thermal Stability after Irradiation	Drying Behaviour of Paints
Photometry/Light Transmission	Thermal Behaviour of Chocolates
Simultaneous IR-Measurements	Changes in Photoemulsions

Typical heating rates used in simultaneous DSC/thermomicroscopy runs are 1–5 deg/min. Sample weights are of the order of 10–20 mg, depending on the density. The substances used in the present experiments were KNO_3 and $NaNO_3$ (p.a. Merck); diphenylamine and benzophenone; 5-n-heptyl-2-(4-cyanophenyl)pyrimidine and 5-n-heptyl-2-(4-cyanophenyl)pyrimidine.

Table 1 gives a more detailed description of the instrumentation which is required for thermomicroscopic analysis. Besides the microscope, the simultaneously used accessories, such as the hot-stage, photometer and ir spectrometer, can be of special importance. Optical recording of the results with a film or TV camera and processing of the measured data can also be helpful for evaluation of the measurements. Table 2 shows the possible applications of thermomicroscopic analysis with and without DSC, and is subdivided into two blocks according to methods and materials.

Experimental

From the variety of significant applications for DSC/thermomicroscopy, three examples will be discussed briefly in the following:

Potassium nitrate–sodium nitrate phase diagram [1].

From the micro-thermoanalytical investigations by Kofler [2], this system is known to form a continuous series of solid solutions. A special characteristic of these solid solutions, however, is that periodic segregation phenomena occur during heating and cooling. In our experiments, mixtures of KNO_3 and $NaNO_3$ in 5 mole% steps were melted and the corresponding cooling curves were recorded afterwards with DTA. Simultaneously, the crystallization process was observed microscopically

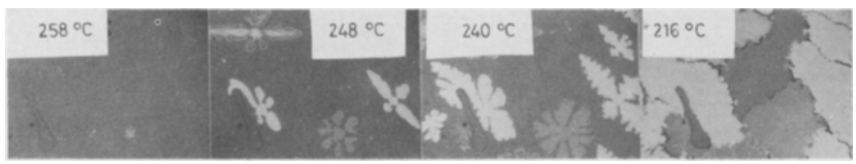

Fig. 4 Microphotographs of the crystallization (160×) of 3 KNO_3 : 1 $NaNO_3$

with the hot-stage. As an example, Fig. 5 shows the DSC cooling curve of a 3 : 1 mixture of KNO_3 and $NaNO_3$. The onset-point of the primary crystallization was determined as 257.5°. This is in good agreement with the microscopic observation that the nucleation of the first crystals occurs at 258° (Fig. 4).

The number of crystal nuclei increases up to about 248°; further cooling to 240° results in pronounced crystal growth, with complete eutectic solidification at 216°.

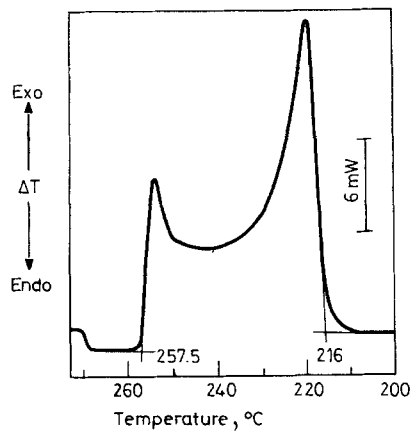

Fig. 5 DSC cooling curve of 3 KNO_3/$NaNO_3$. Sample weight: 24.44 mg, Heating rate: 2 deg/min

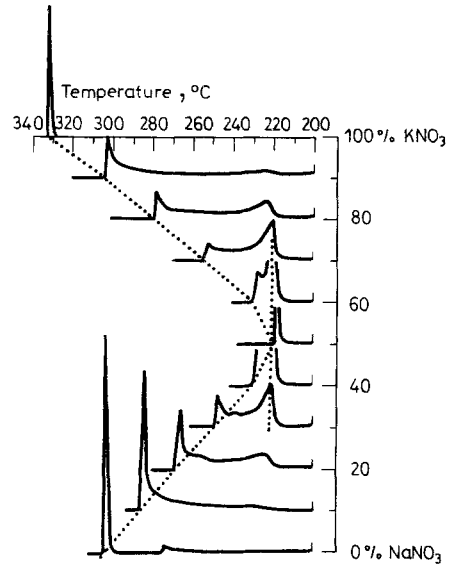

Fig. 6 Phase diagram

Fig. 7 Solidification of the eutectic mixture of the nitrates

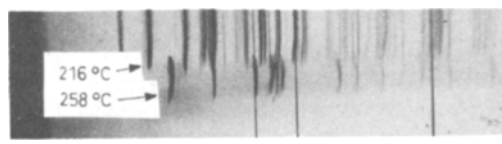

Fig. 8 Heating X-ray photographs of a mixture 3 KNO_3/1 $NaNO_3$

The X-ray heating photograph shown in Fig. 8 is also in excellent agreement with the results of DSC and thermomicroscopy. Figures 4 and 5 prove that the correlation between the microscopically observed crystallization phenomena and the DSC curve is generally very good. The liquidus curve and the eutectic line for the system KNO_3—$NaNO_3$, as determined from the DSC curves, are shown in Fig. 6. These results confirm that this system is indeed a simple eutectic system. It should be

pointed out that it is relatively difficult, however, to determine the exact temperature of the eutectic onset points for mixtures with low concentrations (< 5 mole%) of KNO_3 or $NaNO_3$. A mixture of the nitrates in the eutectic proportion showed typical dendritic solidification after cooling to below 216° (Fig. 7). The β–α transformation of KNO_3 is metastably frozen in at room temperature, independently of the temperature and the cooling rate. In the micrograph the spontaneous transformation which may occur afterwards becomes visible as nucleation.

Diphenylamine-benzophenone phase diagram

Theoretical and experimental investigation on this system [3] are controversial with respect to the existence of an intermediate compound with molar ratio 1 : 1. Figure 9 shows the phase diagram with the experimental values derived from DSC measurements. The liquidus curve is in good agreement with the curve calculated by

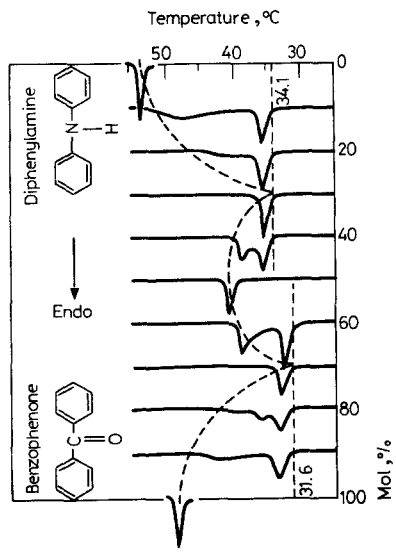

Fig. 9 Phase diagram diphenylamine-benzophenone. Sample weight: 2.1–5.7 mg. Heating rate: 1 deg/min

Björge et al. [3]. Investigations with simultaneous DSC/thermomicroscopy (Figs 10, 11) definitely proved the existence of the intermediate compound, with congruent melting point, and of two eutectics in the system. The temperatures were 34.2° and 31.6° for the eutectic composition with 72 mole% diphenylamine and 28 mole% diphenilamine, and 40° for the intermediate compounds with 50 mole% diphenylamine. All the DSC measurements were carried out during heating to the samples,

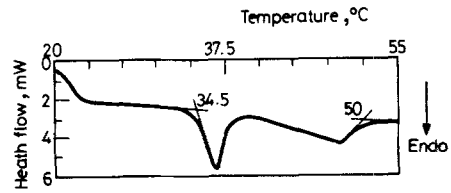

Fig. 10 DSC curve. Sample weight: 5.46 mg. Heating rate: 1 deg/min
Diphenylamin 10 mol%, benzophenone 90 mol%

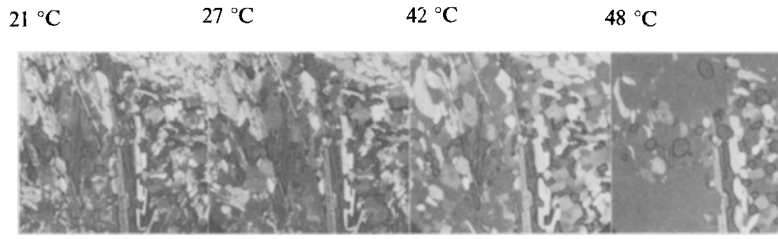

Fig. 11 Microstructures formed during the melting process (see Fig. 9)

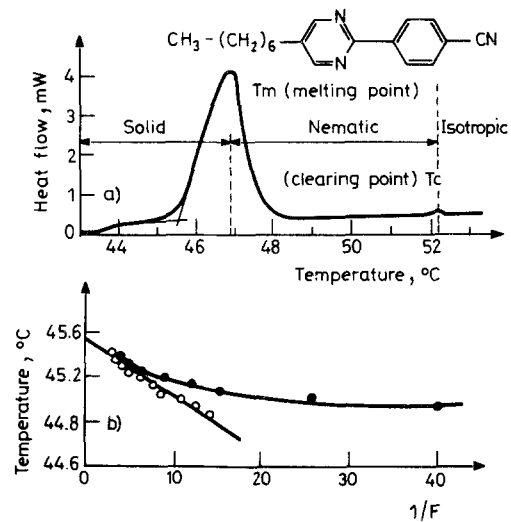

Fig. 12 DSC and purity curves
a) Sample weight: 5.1 mg. Heating rate: 2 deg/min
b) 5-n-heptyl-2-(4-cyanophenyl)-pyrimidine. Purity: 99.91 mol% T_0 = 45.59°C

which means that the recorded phase diagram is a heating diagram. Generally, phase diagrams are derived from slow cooling runs. Therefore, for comparison and in order to prove the validity of the phase diagram, DSC measurements simultaneous with microscopy were carried out. The results show that there is a slight displacement of

the liquidus curves, as one might expect. The morphological changes, which are very pronounced, are shown in Fig. 11. They can be perfectly correlated with the onset temperatures of crystallization. Small subsolidus thermal effects which were observed in some of the benzophenone-rich compositions disappeared after equilibration of these samples for about one month at room temperature.

Liquid crystal system between 5-n-heptyl-2-(4-cyanophenyl)pyrimidine and 5-n-pentyl-2-(4-cyanophenyl)pyrimidine [4].

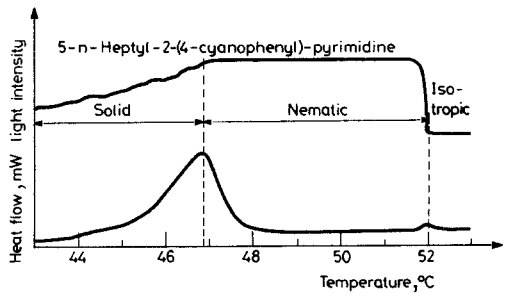

Fig. 13 TDA and DSC curves

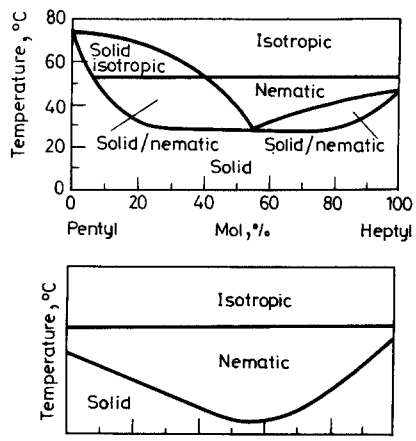

Fig. 14 Phase diagrams

Both these compounds are commercially available liquid crystals with one nematic phase. The eutectic mixture heptyl (40)/pentyl (60) is used in displays for electronic calculators. This phase diagram is studied at present by simultaneous DSC-microscopy, which is ideal for the determination of the thermal characteristics not only of individual liquid crystals, but also of their mixtures.

Figure 12 shows the DSC curve of the pure heptyl liquid crystal with the melting point T_m at 45.6° and the clearing point T_c at 52.2°, which is in fair agreement with the values listed in the specification sheet of the producer. The lower curve in Fig. 12 shows the purity analysis of this liquid crystal, another application of DSC. Besides the purity, the melting point of the pure substance can be determined by extrapolation. The DSC curve can again be correlated with the morphological changes which are observed during heating and cooling. The appearance of the solidified liquid crystal after cooling-down of the isotropic phase is similar to the original solid form. The transformation from the isotropic to the nematic phase is observed at a temperature identical to that determined from the DSC curve. The thermal effects may also be correlated with changes in the light transmittance (Fig. 13).

Since mixtures of the pentyl and heptyl liquid crystals are of commercial importance, the binary phase diagram has been investigated by simultaneous thermomicroscopy/DSC. The results are shown in Fig. 14, where the upper diagram was recorded during heating and the lower one during cooling. This simplified presentation shows a tremendous difference between these two diagrams. For interpretation of these results, further investigations will be carried out.

References

1 W. Perron, G. Bayer and H. G. Wiedemann, J. Thermal Analysis ICTA'80 p. 279, Birkhäuser Verlag, Basel, Boston, Stuttgart, 1980.
2 A. Kofler, Mh. Chem., 86, 4 (1955) 643–652.
3 B. Björge, J. Brynestad und K. Grjotheim, Z. Physik. Chem., 216 (1961) 118–125.
4 A. Boller, M. Cereghetti, M. Schadt and H. Scherrer, Mol. Cryst. Liq. Cryst., 42 (1977) 215.

Zusammenfassung — Die Korrelation zwischen morphologischen Veränderungen und DSC-Kurven ergibt wertvolle Informationen über den Mechanismus von Phasenumwandlungen. Es wird ein neues Gerät zur simultanen DSC und Thermomikroskopie im durchfallenden Licht beschrieben, in dem die DSC-Einheit in einem im Handel erhältlichen hot-stage untergebracht ist. Die Anwendbarkeit dieses DSC/Thermomikroskops wird durch Untersuchung der Phasendiagramme KNO_3–$NaNO_3$, Dyphenylamin-Benzophenon und eines Flüssigkeitskristallsystems demonstriert.

Резюме — Корреляция между морфологическими изменениями и данными ДСК предоставляет ценную информацию о механизме фазовых превращений. В статье описывается новая аппаратура для совмещенного метода ДСК и термомикроскопии светопропускания, в которой ДСК прибор помещен на выпускаемый промышленностью нагревательный столик микроскопа. Применение совмещенного метода ДСК и термомикроскопии показано на примерах фазовых диаграмм для KNO_3—$NaNO_3$, дифениламин-бензофенон и жидкокристаллической системы.