Journal of Thermal Analysis, Vol. 40 (1993) 1031-1040

NEW TA SYSTEM FOR SIMULTANEOUS DETERMINATION OF THERMO-OPTICAL PROPERTIES AND DSC OF DIFFERENT ORGANIC COMPOUNDS

H. G. Wiedemann

METTLER-TOLEDO AG, CH-8606 GREIFENSEE, SWITZERLAND

A new instrument for DSC in combination with thermomicroscopy in transmitted light is described, where a DSC device is in corporated within a commercially available hot stage.

Keywords: new instrument, thermomicroscopy with DSC, thermo-optical analysis

Introduction

Thermoanalytical results e.g. from DSC, are usually reproducible and quantitative, but cannot always be correlated with the respective phase transformation or chemical reaction occurring in the substance. Combining thermomicroscopy with DSC is a very useful and versatile approach because one can then see changes in the investigated substance together with the course of the measured curve.

Instrumental

The simultaneous measurements are based on a commercial microscope and the hot stages FP 82 and FP 84 of the Mettler Thermosystem FP 900 [1–3].

Figure 1 shows the microscope with the hot stage and the control unit, which can be connected directly to a printer or to a personal computer system; in the latter case the DSC and light transmission curves can be displayed simultaneously on the monitor. The sample is loaded directly into a sapphire crucible. In the case of low-viscosity substances and of liquid crystals, three sapphire balls act as spacers and help to maintain uniform sample distribution and thickness during measurement.

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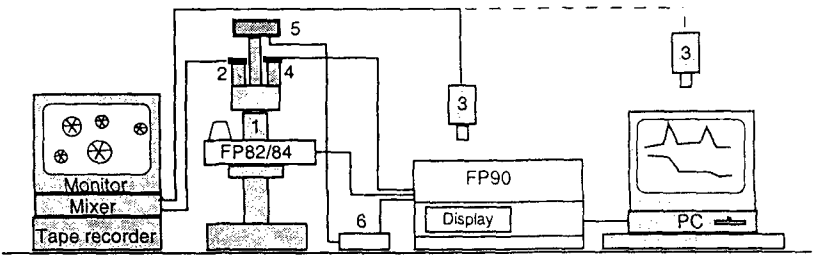

Fig. 1 Thermo-optical station: 1: microscope, 2: video camera (1), 3: video camera (2), 4: photomonitor, 5: camera, 6: handset

The FP 900 system

The Mettler FP 900 thermosystem comprises a central Processor and and several measuring cells for the determination of a wide range of thermal data. The temperature of the attached cell is measured by a precision sensor.

The FP 90 central processor is a control and evaluation unit for the measuring cells, any one of which can be attached without the need for temperature recalibration. The measurement parameters are entered in dialogue with the 6-line liquid crystal display on the keypad of the control unit. After measurement, results appear on the alphanumeric display and can be documented with an optional dot matrix printer.

It is also possible to display the information in analogue manner (light transmittance, or DTA curve as a function of temperature). Experimental data can be transferred to a computer via a standard interface (RS 232C) and there stored and processed further.

Application of the FP 900 thermosystem is based on computer menus. The main menu is shown in Fig. 2. For selecting the mode (DSC, transmission), temperature program or other functions the corresponding function keys are

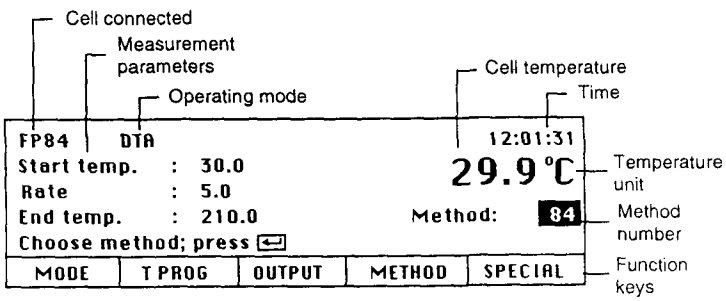

Fig. 2 Main menu

pressed. The output key activates the printer (and elapsed time depending on heating rate), the method key stores the experimental data, and the special key is used for calibration. Figure 3 shows typical graphical displays: the upper one corresponds to light transmission measurements of a compound as a function of temperature and time (FP 82), the lower shows the DSC curve as a function of temperature and time measured with the FP 84. The function keys allow for instance acceleration of the temperature gradient during measurement (fast) or cancellation of a measurement by reset. By use of external video cameras it is possible to mix the graphic display with the microphotograph of the substance on the monitor and to store this combined information with a tape recorder (Fig. 1).

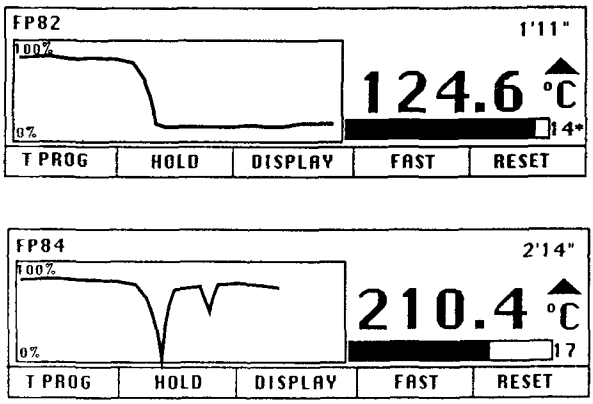

Fig. 3 Two displays of different curves. A transmission measurement (FP 82) and a DSC measurement (FP 84) with the corresponding temperature and other information

The FP 82 hot stage

The FP 82 hot stage is shown schematically in Fig. 4. The sample under investigation is placed between a slide and a cover glass using the method normally employed in microscopy. The sample is subjected to a temperature program and observed visually, photographed or filmed using a video camera.

An optional photomonitor allows quantitative determination and plotting of the light intensity of the field of view. The hot stage together with the upper heating plate can be flipped up to allow free access to the sample chamber.

Microscopes and stereo magnifiers which fulfil the following requirements, can be used with the FP 82 hot stage:

– The distance between the front lens of the objective and the stage must be greater than 29 mm when the stage is lowered completely or the body tube is fully raised.

– The free working distance of the objective must be at least 7 mm.
– Objectives with a working distance of less than 12 mm should have a maximum size of 19 mm so that they fit into the opening of the outer casing.
– Magnification greater than 250× is possible only with special objectives.

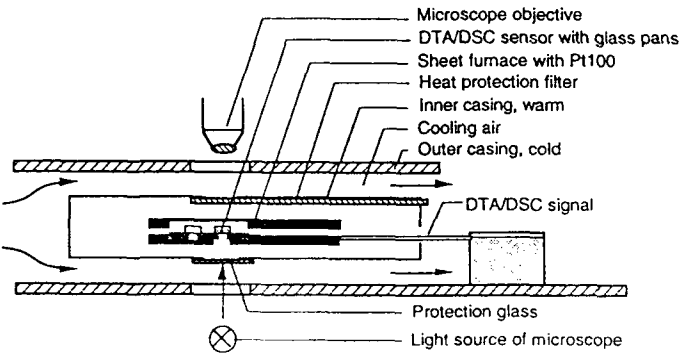

Fig. 4 Schematic cross-section through the FP 82 Microscope Hot Stage

The FP 84 hot stage

Instead of the slide in the FP 82 hot stage, the FP 84 has a DTA/DSC sensor. The sample is placed in a transparent crucible and, together with an inert reference crucible, is subjected to a temperature program. The sample is observed visually, photographed or filmed by video camera. An optional photomonitor allows determination and recording of the light intensity of the field of view. The mesuring sensor with transparent sample and reference crucibles is located in the centre of the furnace and is heated from both below and above so that temperature gradients are kept to a minimum. The DTA/DSC measuring principle is shown in

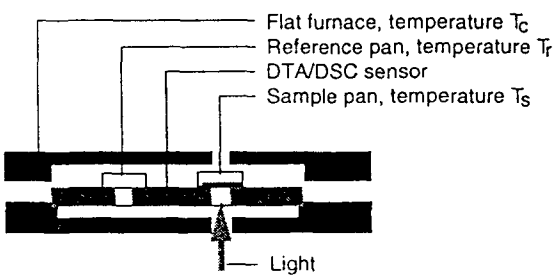

Fig. 5 DTA/DSC measuring principle

Fig. 5. The measuring cell, which is built into the flat furnace, carries the transparent sample and reference crucibles.

Experimental

Phase transformation and melting of substituted PET

The photographs (Fig. 6) of single crystals of substituted PET, dimethyl 3,6-dichloro-2,5-dihydroxy-terephthalate [4], were taken on the hot stage of the microscope. Isothermal heating at 118.9°C, the temperature of the beginning of the phase transition, leads to a colour change from yellow to white due to rotation of the molecules. This gives rise to cracks and fissures which can be seen in their storage of growing (118.5°C). The melting point of this substituted PET (Fig. 7) is strongly reduced to about 180°C compared with 235°C for non-substituted PETP. During cooling the crystallization of the yellow modification starts at 164.6°C. Slow cooling rates (0.1 deg·min^{-1})lead to the formation of a single crystal whereas rapid cooling (10 deg·min^{-1}) results in a polycrystalline aggregate due to undercooling.

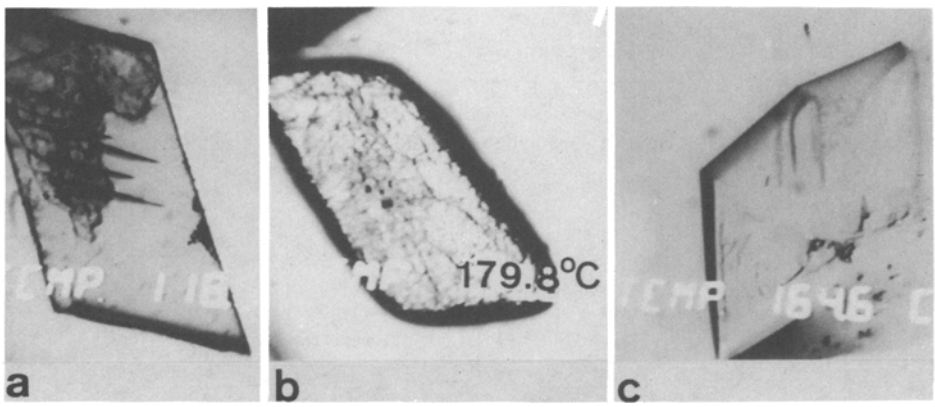

Fig. 6 Microphotographs of substituted PET, during phase transition (*a*), melting process (*b*) and the single crystal crystallization (*c*)

Crystallization of melt-quenched sulfapyridine

For these experiments a sample of sulfapyridine was heated to above the melting temperature (193°C) and quenched in liquid nitrogen. During linear heating

(5 deg·min^{-1}) the DSC curve (Fig. 8) shows the glass transition at ~60°C, a strong first crystallization peak at ~100°C followed by a weak second crystallization at ~140°C and an endothermic melting peak at 193°C. Thermomicroscopic investigations prove, that during the first crystallization peak the amorphous material assumes a polycrystalline microstructure, which changes to a coarse crystallized lath-like structure during the second crystallization peak (Fig. 9).

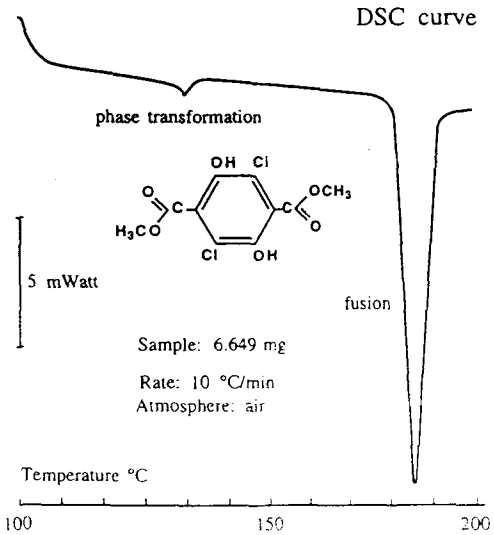

Fig. 7 DSC curve of dimethyl-3,6 dichloro-2,5-dihydroxyterephthalate

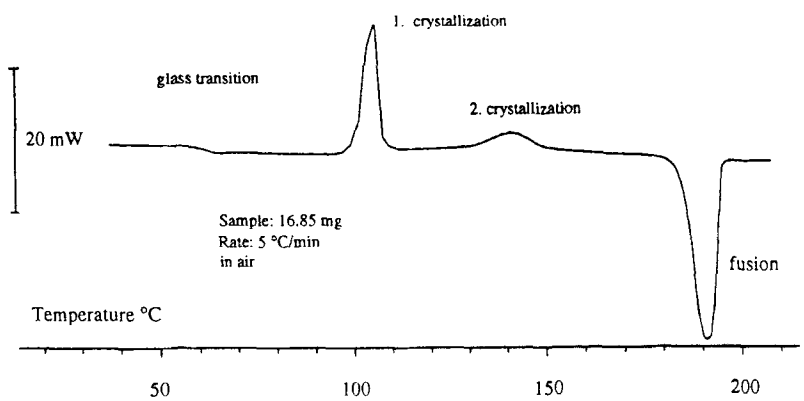

Fig. 8 DSC curves of melt-quenched sulfapyridine

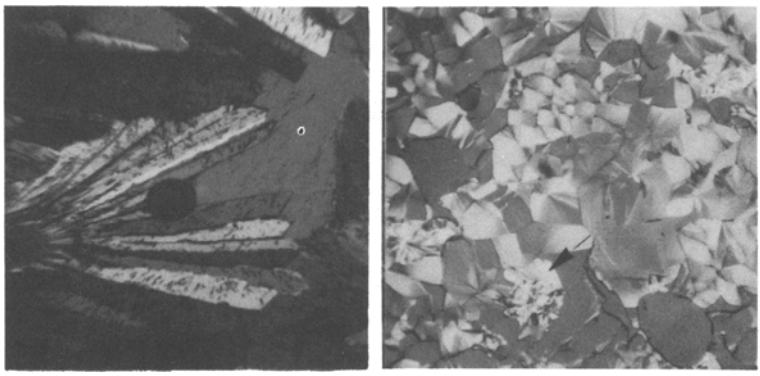

Fig. 9 Microphotographs of the different phases of sulfapyridine

Phase transitions in a liquid crystal (TBBN)

Figure 10 shows a DSC curve and a thermo-optical analysis (TOA) curve (transmission) of a liquid crystal. Measurements were carried out on a crystalline powder of the unheated compound. The first peak corresponds to melting (T_m). The second peak is related to the transformation into a new liquid crystal phase, followed by a glass transition (T_g). Above the transition temperature of 198.7°C a nematic phase appears. Finally, at 234.4°C the clearing point T_c is observed. The simultaneously measured thermo-optical analysis (transmission) supports these findings. The TOA curve shows the different transitions by very pronounced sig-

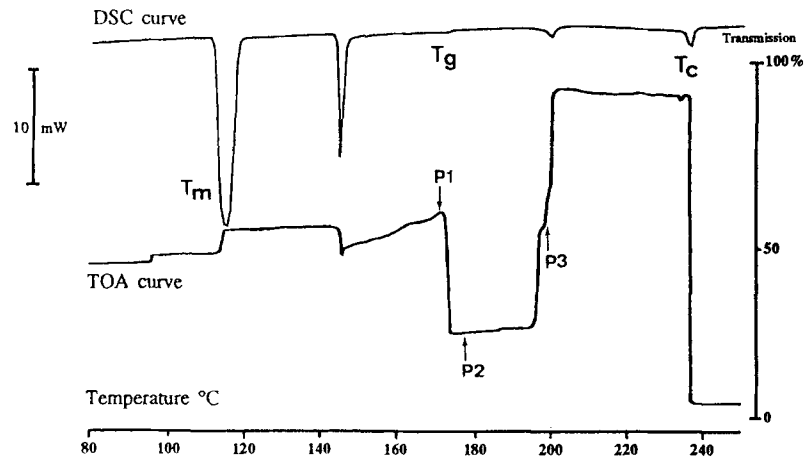

Fig. 10 DSC and TOA curve of a liquid crystal (TBBN)

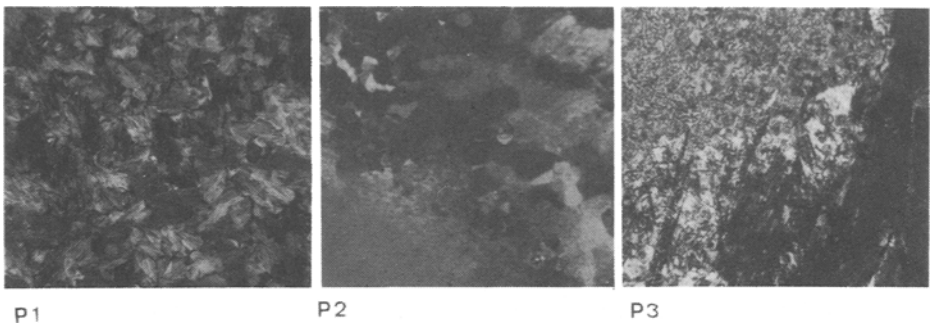

Fig. 11 Micrographs of a liquid crystal (TBBN)

nals, whereby processes can be observed, which are not detectable in DSC measurements. Some microphotographs are shown in Fig. 11, to illustrate morphological characteristics at different temperatures.

Storage effect on the stability of phenobarbital crystals

The standard DSC curve (Fig. 12*a*) of freshly produced phenobarbital shows two melting peaks, one due to the thermodynamically unstable compound (extrapolated onset 172.5°C) and one due to the thermodynamically stable compound (onset 175.4°C). After storing the same sample for about six months at room temperature, the DSC curve shows only the thermodynamically stable compound (Fig. 12*b*). In a melt-quenched sample of the phenobarbital, two different types of crystals form (Fig. 13), spherulites and lath-like crystals. These represent the two

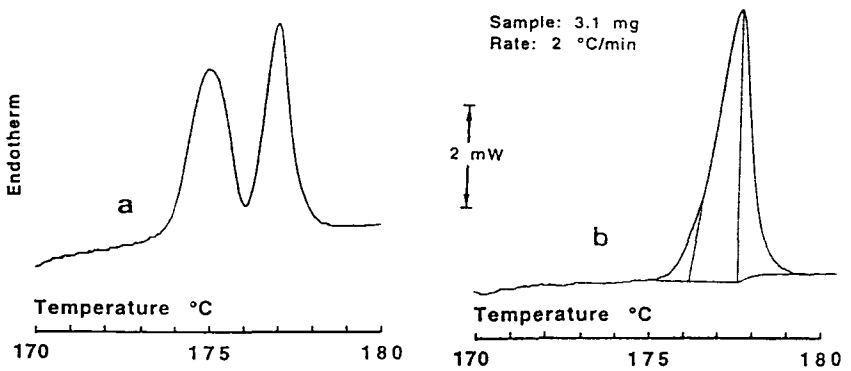

Fig. 12 DSC curves of phenobarbital, *a*) stable and unstable compound, *b*) stable compound

different modifications. The bubbles developed during the melting process of the thermodynamically stable compound could be correlated with vaporization.

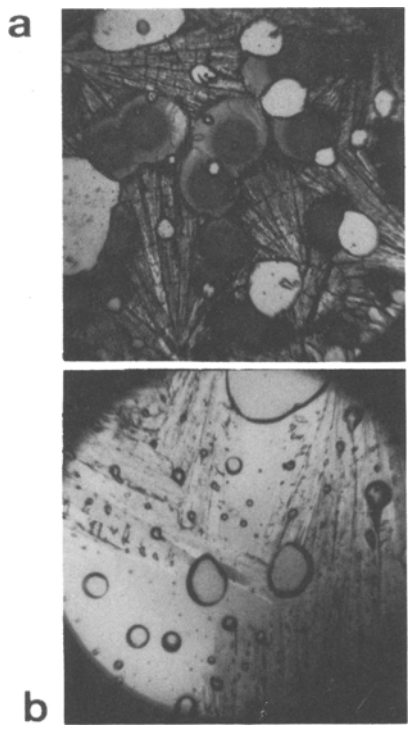

Fig. 13 Microphotographs of phenobarbital, *a*) stable and unstable compound, *b*) unstable compound

Conclusions

New thermoanalytical methods such as simultaneous measurement of DSC and thermo-optical observations allow new insight and interpretations of the effects of temperature on physical properties of materials. The use of new thermoanalytical devices and modern TV-techniques offer possibilities of the visualization and correlation of microstructural effects as a function of time and temperature.

References

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Zusammenfassung — Es wird ein neues Gerät für DSC in Verbindung mit Thermomikroskopie in durchfallendem Licht beschrieben, in dem in einem handelsüblichen Mikroskopheiztisch eine DSC Vorrichtung untergebracht wird.