METHODICAL ASPECTS IN THERMAL ANALYSIS OF LIQUID CRYSTALLINE SUBSTANCES

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On the basis of experience in liquid crystal research, the optimum conditions are presented for the use of thermo-microscopy and microcalorimetry (DSC) in preliminary investigations of the general chemical, thermodynamic and kinetic behaviour. In the second step, special measurements are necessary to obtain exact results on purities, phase types, temperatures, enthalpies, and kinetic parameters of transitions in stable and metastable states.

In spite of the advances in theoretical knowledge about the relations between the chemical structures and physical properties of liquid crystals [1], in investigations of new materials of technical importance empirical research methods are still in use, and many substances are developed which have to be characterized as quickly as possible. The main methods, microscopy and microcalorimetry, are well able to yield information on purity, chemical stability, and stable and metastable phases in the solid and liquid states, etc. [2–5]. Our following remarks may help to avoid drastic mistakes in operation and interpretation, and to optimize the conditions in the starting investigations, in order to obtain maximum information at minimum expense of substance and time. First, preliminary investigations have to be carried out with a combination of microscopy and microcalorimetry; later, special measurements should follow, possibly complemented by other, more expensive methods, e.g. X-ray structural analysis.

Preliminary investigations

Numerous fundamental properties can be recognized by a trained eye through the use of a *microscope* equipped with crossed polarizers and a heating-cooling stage [2]. In the heating-cooling-heating procedure, the textures give hints on the phase types [4] and transitions, on decompositions at higher temperatures, and on supercooled states with "monotropic" phases. Special difficulties exist in connection with solid modifications and transitions in which texture changes are missing ("paramorphosis"). In these cases, *calorimetric* investigations should be started without delay. These

usually clarify the situtation, so that repetitions of microscopic studies are required only after unsuccessful calorimetric runs. A sample of 2–3 mg of original substance, not previously heated up, is annealed in the DSC at minimum temperature for a few minutes, then heated up into the isotropic state, cooled down, and heated up again at a rate of 10 deg min^{-1} in each case. The heating should be stopped below the onset of any decomposition, known from previous microscopic observation or detected from irregular baseline deflections.

In comparisons of microscopic observations with peaks in the respective calorimetric curve, the results can be classified into the following groups:
— peaks observed with both methods,
— peaks observed only under the microscope ("weak" transitions),
— peaks measured only by DSC ("paramorphosis").
From a kinetic point of view, there are transitions [6]:
— without significant hysteresis ("fast" transitions),
— with considerable hysteresis ("hindered" transitions),
— observed only in the first heating run (low-temperature solid, stable solid modification),
— observed only in cooling runs ("monotropic" phases),
— observed only in the second heating run (metastable modifications) [7].

Special investigations

Generally, the successful performance of a special investigation depends on the parameters necessary for theoretical or technical application, but we recommend that the approved sequence be followed on the way from fundamental to complex investigations. First *"weak" transitions* should be treated. Examples of such transitions with small enthalpies are smectic G — smectic F and cholesteric-blue phase, first observed optically, or smectic A — smectic Ã and the restacking transitions between different smectic B phases, first found by means of X-ray analysis [1, 8]. Heavy samples of up to 30 mg of well-purified material have to be measured in a temperature interval of 20 deg on both sides of the expected point. The best resolution will be obtained at a heating-cooling rate of 10 deg min^{-1} with perfect thermal contact between the sample pan, and the sample holder, and with balanced heat capacities of sample and reference. In this way, transition enthalpies of 10 mJ/g can be detected (Fig. 1, see also [1, 8], demonstrating the high DSC sensitivity, comparable with that of the best adiabatic instruments [9], which require a three orders of magnitude higher
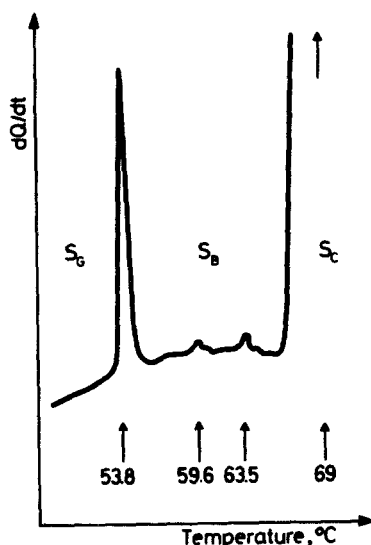
Fig. 1 DSC curves with restacking between smectic B phases of heptyloxybenzylidene-heptylaniline.
(Perkin—Elmer DSC-2, 7.4 mg, 5 deg min⁻¹)
hexagonal AAA-orthorhombic F 59.7 °C
orthorhombic F-hexagonal ABAB 63.5°C.

expenditure of substance and time and have a one order of magnitude better temperature accuracy.

Next, *the types of liquid crystalline phases* should be identified via micro-scopically observed textures, through conclusions from homologous substances, and mainly from miscibility investigations with phases of reference materials, a complicated and time-consuming procedure, also supported by X-ray analysis [1, 4]. The precise determination of *transition temperatures* then follows. In the case of fast transitions, the peak maximum temperatures of a series of heating runs with decreasing rates are extrapolated to thermal equilibrium. For melting points and other transitions with hindered reversion, a virgin sample can be hated up as slowly as possible in the transition region, to avoid essential temperature lags, or, if a bigger error may be accepted, the slope onset temperature of runs at a higher heating rate can be used. If any purity analysis is intended, a melting temperature too will result. In some cases, a 0.2 deg error has been achieved, but 0.5 deg is common for sharp transitions in routine operation.

For the precise determination of *transition enthalpies,* three virgin, carefully weighed samples are used, each of them annealed at transition onset till any caloric effects are absolutely relaxed. After the DSC run at 10 deg min⁻¹ (orr less, if different transitions remain close) is finished, the sample

mass should be compared with the initial value. The error is caused by the instrumental calibration accuracy, the straggling of the results, the errors of the balance, the impurity content and the integration error. A total of 1% is possible, but 5% can be assumed in common routine operation. In transitions of liquid crystalline phases, homogeneous pretransitions may exceed the latent effects, and baseline constructions [10] are more or less arbitrary because of the curvature in the specific heat in the "weakly first--order" transitions, playing a dominant role for error sources. *First and second-order transitions* can also be differentiated by means of a series of DCS curves [11].

Purity analysis can be performed by dividing the continuous melting peak into partial areas [5] or by stepwise heating of the sample. We prefer the latter, to be certain that the melting equilibrium is established. Recently crystallized material can result in better values than old samples. An impurity content between 0.1 and 10 mol% can be well analyzed in the case of a miscibility gap in the solid state. This amount is found to be too small if the impurity resembles the main substance. Deviation of the results in different regions of the same melting curve indicates that several solid modifications exist, making a reliable purity determination nearly impossible.

Microcalorimetry allows resolution of the *dynamic behaviour* of transitions within the time scale between 10 to 10^3 s by direct determination of caloric effects, and by indirect methods for longer times. Most transitions
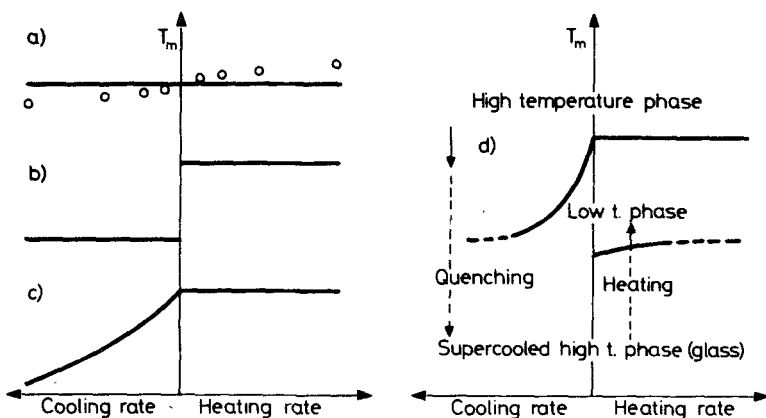
Fig. 2 Kinetic behaviour of phase transitions (schematic diagram),
Peak maximum temperature T_m vs. heating/cooling rate, ○ measured values, ▬ instrumental lag corrected, a) fast transition, b) hindered nucleation and fast crystal growth, c) hindered crystal growth, d) after quenching (↓): a supercooled phase exhibits on heating (↑) exothermal and endothermal transitions.

connected with liquid crystals occur much faster, but in some cases strong hindrances could be observed, as in transitions into solid phases [12]. In the isothermal method, which is well adapted to the Avrami equation, calorimetric curves at constant supercooling or overheating are plotted vs. time. The dynamic method is more common for empirical descriptions of complex hysteresis effects. Here the maximum transition temperatures of different DSC runs are plotted vs. heating-cooling rates, providing information on nucleation, crystal growth and glassy freezing (Fig. 2).

References

1 D. Demus, S. Diele, S. Grande and H. Sackmann, Advances in Liquid Crystals, 6 (1983) 1.
2 L. Kofler and A. Kofler, Thermo-Mikro-Methoden zur Kennzeichnung organischer Stoffe und Stoffgemische, Vlg Chemie, Weinheim 1954.
3 W. Hemminger and G. Höhne, Grundlagen der Kalorimetrie, Akademie Vlg, Berlin 1980.
4 G. W. Gray and J. W. Goodby, Smectic Liquid Crystals, Lionard Hill, Glasgow 1984.
5 G. M. Gustin, Thermochim. Acta, 39 (1980) 81.
6 A. Wiegeleben, D. Marzotko and D. Demus, Cryst. Res. Technol., 16 (1981) 1205.
7 H. Hartung, U. Baumeister, M. Jaskolski, A. Mädicke and A. Wiegeleben, Cryst. Res. Technol., 21 (1986) 1.
8 A. Wiegeleben, L. Richter, J. Deresch and D. Demus, Mol. Cryst. Liqu. Cryst., 59 (1980) 329.
9 J. Thoen and G. Seynhaeve, Mol. Cryst. Liqu. Cryst., 127 (1985) 229.
10 M. J. Richardson, Anal. Proc., 17 (1980) 228.
11 P. Navard and J. M. Haudin, J. Thermal Anal., 29 (1984) 405.
12 D. Demus, D. Marzotko, N. K. Sharma and A. Wiegeleben, Cryst. Res. Technol., 15 (1980) 331.

Zusammenfassung — Ausgehend von den Erfahrungen auf dem Gebiet der Flüssigkristalle wird der optimale Einsatz von Thermomikroskopie und Mikrokalorimetrie (DSC) für allgemein-chemische, thermodynamische und kinetische Voruntersuchungen beschrieben. In einer zweiten Untersuchungsphase sind spezielle Messungen notwendig, um exakte Ergebnisse bezüglich Reinheit und Phasentypen zu erhalten sowie Temperaturen, Enthalpien und kinetische Parameter von stabilen und metastabilen Zustandsänderungen zu bestimmen.

РЕЗЮМЕ — Представлены оптимальные условия использования микроскопии и микрокалориметрии (ДСК) в предварительных исследованиях общего химического, термодинамического и кинетического поведения жидких кристаллов. На последующих стадиях исследования необходимы специальные измерения для получения точных данных о чистоте, фазовом составе, энтальпии, кинетических параметрах и температурах переходов в стабильное и метастабильное состояния.