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# Liquid Crystals, DSC and Thermomicroscopic Investigations

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## INTRODUCTION

In science and technology the use of crystalline liquid substances has undergone an interesting developement during the last years. This is especially the case in the field of electro-optics (liquid-crystal-displays).

The present paper gives some examples of the use of the Mettler Thermosystem FP800/84 for the determination of thermal characteristics of liquid-crystals. These are correlated with the optical behaviour, which is determined by means of microscopy or microphotography.

Crystallized substances generally become liquid at a temperature, the melting point (Tm), that is specific for the substance. hereby an isotropic phase is formed. Liquid crystals, however, do not go during melting from the anisotropic solid state into the isotropic liquid state but first from an anisotropic liquid phase. At a higher, well defined temperature, called the clearing point (Tc), (Tc), the turbid liquid-crystalline phase becomes isotropic-liquid.

## THEORETICAL ASPECTS

In crystallography the term anisotropy is applied to crystals, which show a different growth and structure in the different crystallographic axis, which leads to differences in the physical properties. With liquid crystals it is similar; they behave like optically anisotropic, double refracting liquids. This anisotropy comes from a long-range order of e.g. rod like molecules in the liquid phase. which at the same time they show a mechanical mobility.

A structure generally consists of isotropic or anisotropic building blocks. These can possess translational (T) or rotational (R) degrees of freedom of motion. Rotational degrees of freedom make only sense with anisotropic building blocks. Solid crystals which consist of isotropic building blocks (abbrevation: To x R2) have no degree of freedom. Liquid crystals, on the other hand, consist of aniso-

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tropic building blocks. The smectic structure (T2 × R2) therefore has two translational and rotational degrees of freedom. The cholesteric structure corresponds to T3 × R1, the nematic to T3 × R2 and the isotropic structure corresponds to T3 × R3. In principle there is a deficiency of a translational order. Here, however, exists an orientational order, this means a rotational order related to the elongated axis of the molecule (fig. 1).

About 0.5% of the organic compounds form liquid crystals. These are compounds with elongated molecules of 20-30 Å in length and an axial ratio of 1:4 to 1:8, with fixed axis by double bonds, with strong dipoles in the elongation axis and with easily polarizable groups. As intermolecular forces then act the dipole-dipole attraction, between the permanent dipoles, the induced dipoles and the dispersion forces.
About the thermodynamics of liquid crystals, it can be said that the main portion of the transition enthalpy lies in the first order phase transition between crystal and liquid crystal. For the transition enthalpy from liquid crystal to isotropic liquid only about 2% of the total amount of heat is required. Due to the weak interaction forces, which maintain the liquid crystalline order,

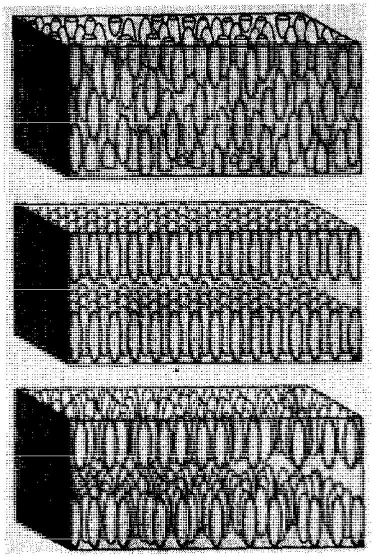


Fig. 1 Arrangement of molecules in liquid crystals, a) nematic structure, b) smectic structures.

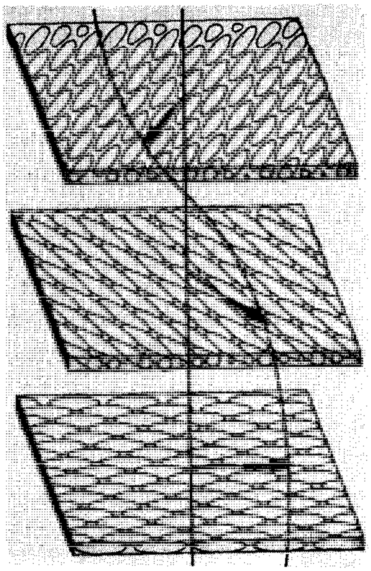


Fig. 2 Helical orientation of the molecular layers of the cholesteric structure.

it is easy to change it by means of external forces like: electric- and magnetic fields and effects on the boundary layers.

This causes different electro-optical effects:
-In nematic phases a dynamic scattering effect occurs. This effect is used for electronic displays.
-In cholesteric phases (fig. 2) a selective reflection of light with a strong color change appears if the helic pitch of the molecular layers changes by thermal- or other influences. This effect is mainly used for temperature indicators in thermography.

A characteristic cholesteric phase appears only with substances that are optically active. The name was chosen, because many derivatives of cholesterin show properties that are characteristic for this phase. As mentioned before, the mobility of the molecules of the cholesteric structure is similar to the nematic structure. In comparison to the nematic structure, however, also a three dimensional structure is formed. This structure has a helical character. The pitch of such a helix is about 0.1 - 10 µm and is substance- and temperature-dependent. Moreover the helix pitch is changed easily by electromagnetic fields, foreign molecules and other influences. The helix can have a right-hand as well as a left-hand screw axis.

The close relationship with the nematic phase becomes evident from the fact, that when mixing right-hand helixes with left-hand helixes, nematic phases are formed depending on concentration and temperature. Besides it is found, that electromagnetic fields interfere with the helix pitch and can even eliminate the helix structure. Hereby nematic phases are formed. Investigations have shown that already a small amount of an optically-active non-nematic substance added to a nematic phase can induce cholesteric properties.

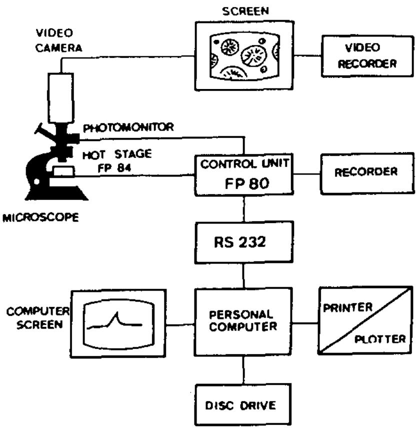
Another structure of liquid crystals that has not been discussed so far is the smectic structure (greek: smectic = like soap, greasy). Here the molecules are arranged in parallel layers; these molecular layers may be shifted perpendicular to the elongated axis of the molecule. Until now no practical applications for the smectic liquid crystals have been found.

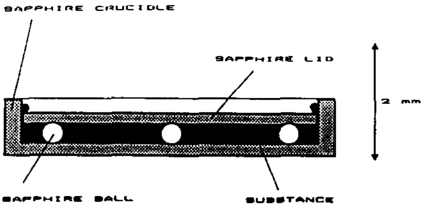
## Experimental part

The experimental set-up for the investigation of liquid crystals is shown in fig. 3. The upper part of the figure shows the microscope with the FP84 TA Microscopy Cell and the FP80 control unit with central processor. For the simultaneous recording of DSC-curves a recorder is used. It is also possible to measure or to record the transmittance of a sample during the thermal treatment (Fig. 5).

The FP80 control unit has a RS 232 output and is connected by means of an appropriate interface to a personal computer. The results presented hereafter were recorded and evaluated with a HP 86B. Depending on the computer configuration, the curves can be plotted or stored in the memory. Listings of the programs can be obtained from the authors.

The sapphire crucible with sapphire lid for holding the sample is shown in fig. 4. Between the bottom and the lid, sapphire balls are used as spacers in order to avoid that liquid crystals are pressed out of the crucible when they reach the isotropic (liquid) state.





↑Fig. 4 Crucible arrangement for the investigation of liquid crystals in the liquid state

← Fig. 3 Experimental set-up for DSC and thermooptical analysis of liquid crystals

The image recording of the structural or morphological changes of the sample by means of a video system can be of great value for the evaluation of the results and for the correlation with the recorded curves. By means of a second camera the corresponding temperatures can be recorded on the same video tape. (Most microscopes are nowadays compatible with video systems.)

## Results and Discussions

### N,N′- bis (4-octyloxybenzylidene)-p-phenylendiamine (OOBPD)

Three DSC-curves of N,N′- bis (4-octyloxybenzylidene-p-phenylenediamine (OOBPD) are shown in fig. 6. The first curve was obtained with crystals from the solution, the second curve with a premelted sample. Both curves show significant differences especially in the shape of the peak and in the course of the baseline. The differences are likely to have been caused by different packing densities of the sample in the crucible, which resulted in a different heat flow in the samples. An earlier publication [1] assumed the following phase transitions:

X 160 S 209 N 238 I

hereby denotes X the crystalline, S the smectic, N the nematic and I the isotropic phase. The indicated values correspond to the temperatures of the phase transitions. In a later publication [2] it is shown, that besides several crystalline phases also different smectic phases occur:

$X\ 115\ S_5\ 142\ S_4\ 149\ S_3\ 155\ S_2\ 164\ S_1\ 203\ N\ 231\ I$

For comparison purposes the different mesophases are indicated in the second DSC-curve (fig. 6). The corresponding temperatures of the phase transitions and the thermodynamic values are presented in the table below:

| Transitions: | T(C) | Delta H (KJ/Mole) | Delta S (J/K Mole) |
|---|---|---|---|
| X - S5 | 115 | 17.6 | 45.6 |
| S5 - S4 | 142 | 6.7 | 16.3 |
| S4 - S3 | 149 | 2.1 | 5.0 |
| S3 - S2 | 155 | 0.4 | 1.0 |
| S2 - S1 | 164 | 3.2 | 7.1 |
| S1 - N | 203 | 3.6 | 7.5 |
| N - I | 231 | 2.3 | 4.6 |

Figure 5 shows the changes in light transmittance during the heating and cooling periods. A series of characteristic microphotographs of OOBPD is presented in figure 7. The numbers of the photographs correspond to the numbers in the figure 5. Comparison of microphotographs 1-4 shows, that the original crystal boundaries are maintained almost until the melting starts. The course of the cooling curve (fig. 5) shows, that the phase transitions I to N and N to S1 are principally reversible [3].

Figure 5: Changes in transmittance of OOBPD during the heating and cooling. The different phases of the liquid crystal are identified on the graph.

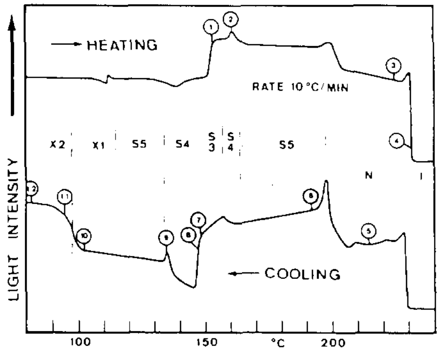
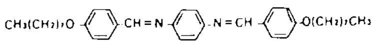
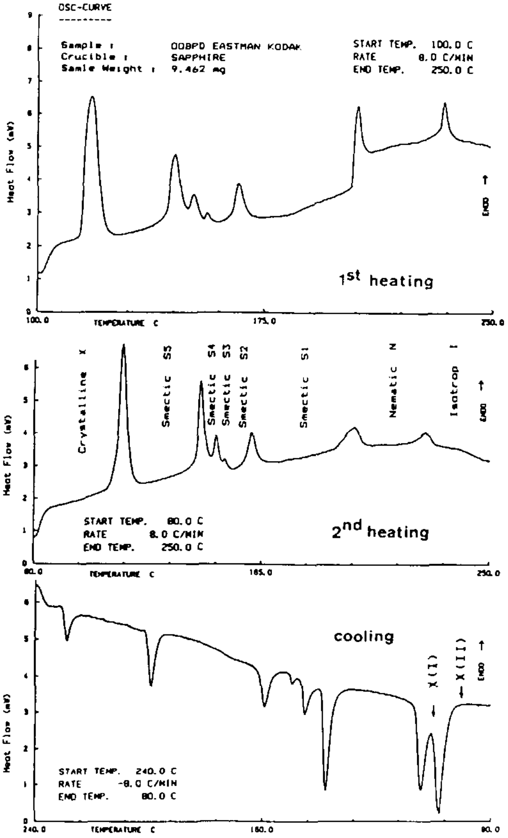


Figure 6. Different DSC-curves of OOBPD recorded during heating and cooling. The first curve was taken with crystals from the solution, the second curve was taken with the premelted sample. During cooling an additional solid-solid transition occurs. This transistion does not take place during heating. Also the transition is visible on the microphoto.

*N,N'*-Bis(4-octyloxybenzylidene)-*p*-phenylenediamine (OOBPD)





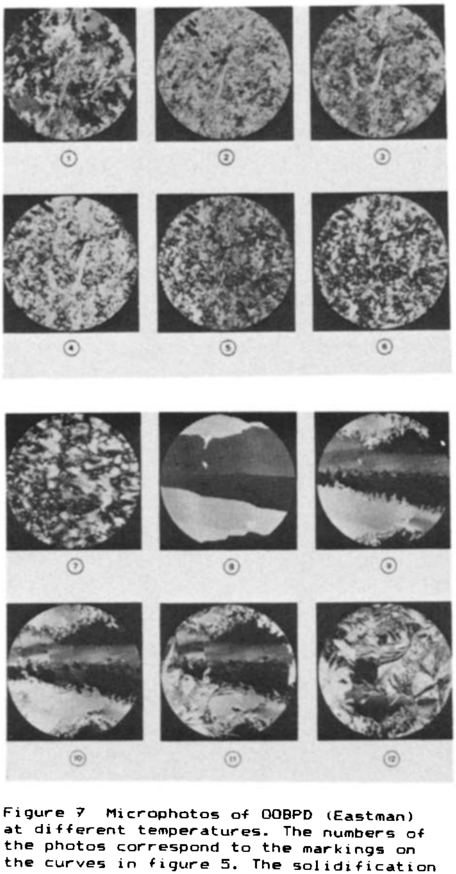


Figure 7 Microphotos of OOBPD (Eastman) at different temperatures. The numbers of the photos correspond to the markings on the curves in figure 5. The solidification S5 to X(II) is in accordance with a rearrangement of the crystal habit followed by a solid-solid transition. Hereby also cracks are formed. The separation between solidification S5 to X(I) and recrystallisation X(I) to X(II) appears at undercooling. This is done by quenching (see fig.6 the two DSC-peaks around 100°C).

The solidification of S5 to X(II) is in accordance with a rearrangement of the crystal habit, followed by a solid-solid transition Hereby also cracks are formed. The separation between solidification S5 to X(II) and the recrystallization X(I) to X(II) appears at cooling. This is achieved by quenching (see fig.6 the two DSC-peaks around 100 °C).

Another thermal analysis method which may be applied for liquid crystal characterization is the dilatometric expansion measurement with the Mettler TA 3000/TMA 40 for OOBPD recorded during cooling. For this purpose the sample was melted in a cylindrical container which was covered with a piston-like lid. This cell was mounted between the platform and the measuring sensor of the TMA for the dilatometric measurements in function of temperature. The curves in fig.8 correspond to the cooling curve and the first derivative of the cooling curve for OOBPD. The latter shows a strong similarity with the DSC-curve of OOBPD (fig.6). The TMA curves already show qualitatively that the dimensional changes at the transitions liquid crystalline-liquid crystalline and solid-solid differ for several orders of magnitude.

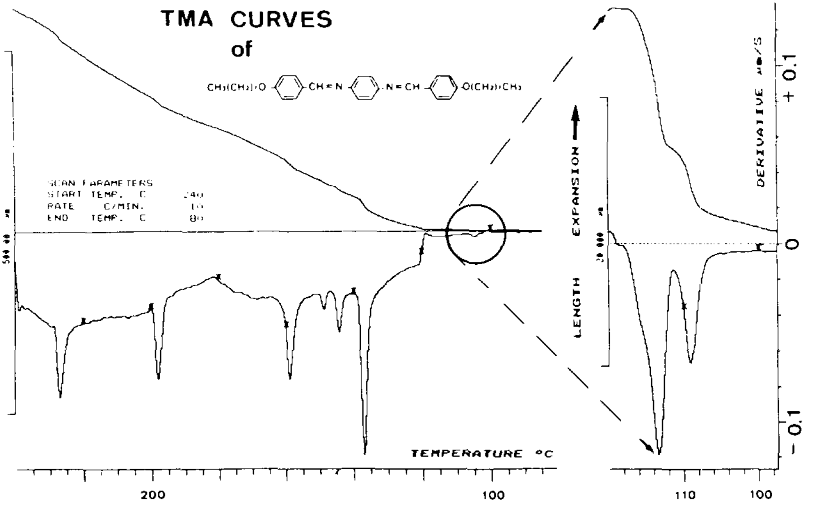
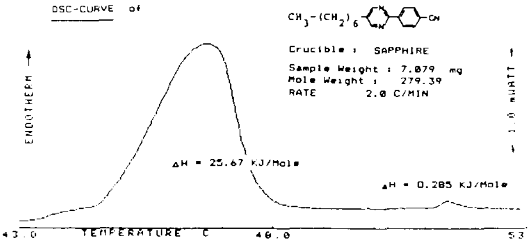
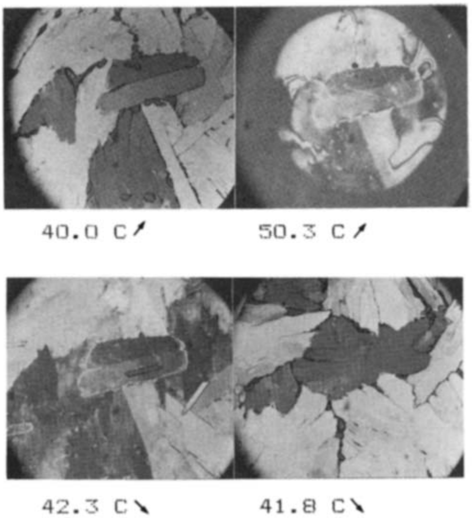


Fig. 8 TMA curves of OOBPD

## 5-n-Heptyl-2-(4-cyanophenyl)-pyrimidine

This compound is a commercially available liquid crystal [4] with one nematic phase. The transition from the crystalline phase X to the nematic phase N lies at 43.5°C, the clearing point at 51°C. This means that at this temperature the compound has become isotropic. According to the temperature range, this would be a typical liquid crystal for the use in displays of calculaters etc. The liquid crystal shows in the range of the nematic phase (48 - 51°C) different interference colors in polarized light. These colors are connected with the expansion during heating, that means with the the thickness of the layer and the double refraction Fig.9 shows the DSC-curve and some microphotographs taken during heating and cooling of the sample. The original appearance of the solidified liquid crystal remains very similar also after freezing from the isotropic phase. The crystallization in the nematic phase at 42.3°C visible. The original appearance of the solidified liquid crystal, however, is different from that of the original material.




40.0 C↗ 50.3 C↗

42.3 C↘ 41.8 C↘

Fig. 9 DSC-curve of 5-Heptyl-2-(4-cyanophenyl) pyrimidine and micro photographs taken at different temperatures

↗ heating ↘ cooling

## Summary

For temperature indicators and for the use in displays of electro-instruments liquid crystals have become extremly important. The growing number of applications requires an accurate knowledge of the phase transitions. These transitions can be examined easily by means of the combined DSC thermooptical analysis method. This simultaneous method is not only an ideal means for the determination of thermal characteristics of liquid crystals but can also be used for the investigations of their mixtures. Since liquid crystals are mainly applied in form of mixtures, this DSC-method is useful also for the determination of the corresponding phase diagrams. The quantitative composition of these mixtures can thus be determined. As typical representatives for liquid crystals the following substances have been studied by simultaneous DSC-thermomicroscopy: OOBPD and 5-Heptyl-2-(4-cyanophenyl) pyrimidine.

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