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Jochen Strauß [a], Andreas Hoischen [a] & Heinz-Siegfried Kitzerow [a]

[a] Department of Chemistry, Faculty of Science, University of Paderborn, Paderborn, Germany

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An Efficient Optical Method to Detect Phase Transitions in Liquid Crystals

Jochen Strauß
Andreas Hoischen
Heinz-Siegfried Kitzerow
Department of Chemistry, Faculty of Science, University of Paderborn, Paderborn, Germany

Phase transitions in liquid crystals can be detected by polarizing microscopy, even if the transition enthalpy is extremely low. We describe an efficient way of transforming microscopic video images to a scalar signal. The temperature dependence of this signal is compared to DSC measurements for two standard compounds. The results indicate that this kind of optical investigation is suitable as a standard tool to measure the transition temperatures of liquid crystals.

Keywords: birefringence; liquid crystals; phase transitions

INTRODUCTION

Liquid crystals are anisotropic fluids which combine fluid behavior and anisotropic properties in a unique way [1,2]. Today, more than 76,000 liquid crystalline compounds and a large variety of different mesophases appearing in these compounds are known [3]. The most obvious anisotropic property is the birefringence which leads to beautiful optical - and in particular electrooptical effects. For more than hundred years, polarizing microscopy has been applied successfully in order to identify the mesophases in new mesogenic compounds and to detect phase transitions. Since the pioneering work by

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Address correspondence to H.-S. Kitzerow, Department of Chemistry, Faculty of Science, University of Paderborn, Warburger Str. 100, 33098 Paderborn, Germany. E-mail: kitzerow@chemie.uni-paderborn.de

Otto Lehmann [4], the basic principle of polarizing microscopy remained the same, but the optical equipment has improved remarkably. On the other hand, the large number of new compounds requires standard methods for a first routine characterization. A few years ago, Coles and coworkers succeeded to detect phase transitions automatically by changing the temperature of the sample continuously and analyzing the video signal of a camera attached to the microscope [5]. More recently other authors suggested similar techniques, analyzing either the signal of a photodiode [6] or the grayscale histogram of microscopic video images [7]. The first method is simple and useful, but not perfect. The second, more sophisticated method analyzes the changes of the image, irrespective of the spatial origin of the pixel data. In our paper, we describe an alternative method to analyze the video signal, making use of a very easy real time algorithm to detect the local change of the image. In spite of its simplicity, the system is very efficient. The procedure is tested for two standard compounds where some phase transitions are difficult to detect by optical and calorimetric studies.

EXPERIMENT

The investigations were carried out with the setup shown in Figure 1, using a SM-LUX-POL microscope (Leitz, Wetzlar) equipped with a 20× lens (Leitz, Wetzlar) and a Hitachi KP-C551 CCD Color Camera. The PAL video signal was digitized in 8 bit grayscale with 720×576 spatial resolution on a MV-Sigma-SLG frame grabber (Matrix Vision). The obtained data were processed at the same time on a 400 MHz PC,

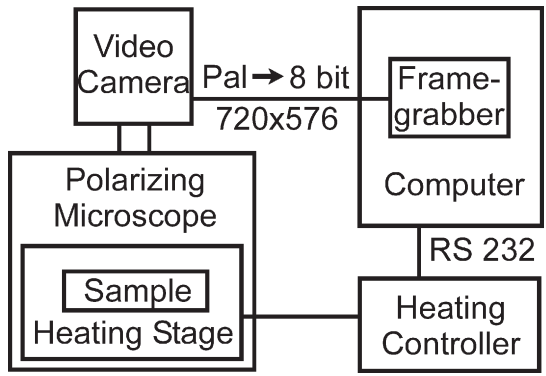


FIGURE 1 Experimental setup.

which was simultaneously reading out the temperature information from the FP90 temperature controller (Mettler) used to drive an FP82 hot stage (Mettler). The sampling rate was limited by the data transfer rate of the temperature controller and was adjusted to give a mean temperature resolution of $\Delta T \approx 0.05\,K$ at temperature scanning rates of 5 K/min and more.

All microscopy samples were prepared from the melt with clean, non-treated microscope slides and cover glasses. The DSC measurements were taken in standard 50 µl aluminum pans on a DSC-2 (Perkin-Elmer) which was modified to allow computerized control and data sampling. The respective temperatures for both methods were determined using the tangential method, where the intersection of the interpolated baseline and the tangential on the rising edge of the peak is identified in order to determine the precise transition temperature.

For our investigations we used two different algorithms to analyze the changes of the image by subtraction of subsequent frames which correspond to two different temperatures, T and (T – ΔT). Figure 2 illustrates the basic idea of our optical method: The digitized image of a typical texture can be represented by a m × n matrix consisting of the grayscale values $g_{m,n}$ of the m × n pixels (in this simple example a 3 × 3 matrix and 3 gray levels). When a phase transition occurs, the distribution of the gray levels and thus the allocation of the matrix changes. Method A quantifies the change in the spatial grayscale information within the image, i.e., the textural changes

$$A(T) = \sum_m \sum_n abs(g_{m,n}(T) - g_{m,n}(T - \Delta T)) \tag{1}$$

whereas method B identifies the integral change in grayscale

$$B(T) = \sum_m \sum_n g_{m,n}(T) - \sum_m \sum_n g_{m,n}(T - \Delta T) \tag{2}$$

Applying these algorithms to the simple example of Figure 2 reveals the difference:

$$A(T) = 12,\ B(T) = 0 \tag{3}$$

While the integral grayscale and the grayscale histogram remain constant, method A returns a non-zero-value, due to the change in spatial grayscale distribution.

To test our method we chose the two compounds 4-octyloxy-thiobenzoic acid S-(4-pentyl-phenyl) ester, "8S5",

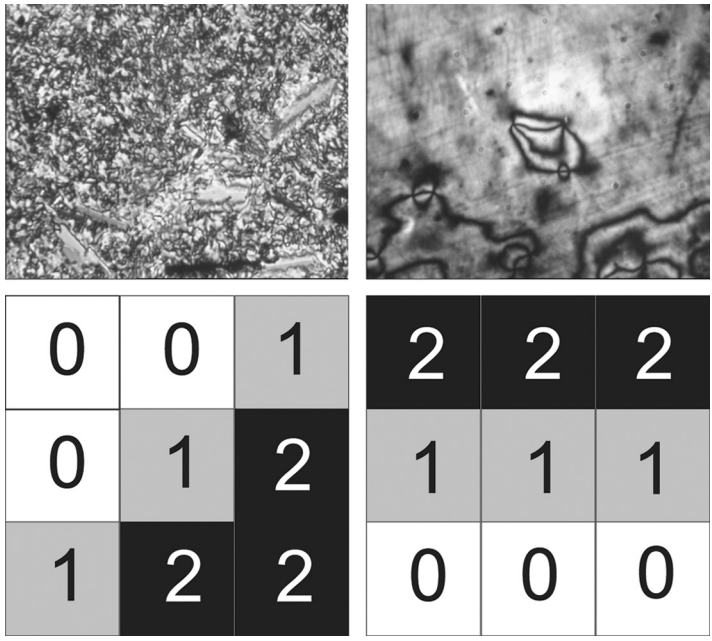
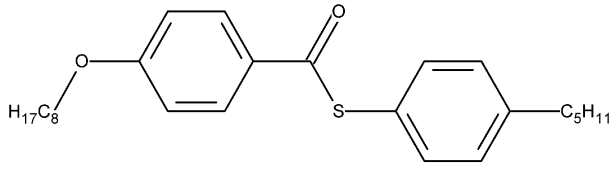
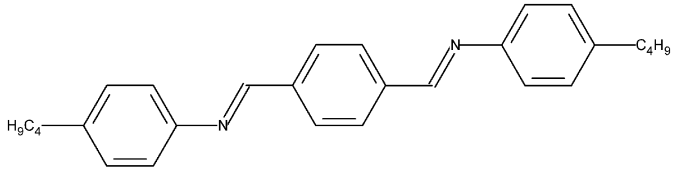


FIGURE 2 Top: Typical images of a solid and a nematic liquid crystalline phase of 8*S*5 in the polarizing microscope. Bottom: Schematic representation of a small area of the respective digital image.



and (N,N′-terephthalydene-bis(4-butylaniline), "TBBA".



Both compounds show a nematic (N) phase and several smectic (Sm) phases. Some phase transitions are difficult to detect in these compounds by standard methods like DSC or polarizing microscopy. The touchstone for the calorimetric method are phase transitions that

TABLE 1 Transition Temperatures and Enthalpies of $\bar{8}S5$, Comparison of the Data Obtained from Optical and Calorimetric Measurements and Literature [3]

Transition	T (°C) Method A	T (°C) Method B	T (°C)/ ΔH (kJ/mole) DSC	T (°C)/ ΔH (kJ/mole) Literature
Cryst. → SmA	57.82	58.14	57.85/33.34	59/34.68
SmA → N	65.21	65.12	62.82/0.05	63/0.09
N → Iso	86.53	86.53	85.79/1.67	86.5/1.3
Iso → N	86.43	86.41	85.73/1.98	–
N → SmA	63.32	62.78	65.11/0.14	–
SmA → SmC	56.11	56.02	59.33/0.08	55.5/0
SmC → SmB	30.69	30.70	29.85/3.03	31/2.89
SmB → Cryst.1	–	–	15.05/4.0	14.4
Cryst.1 → Cryst.2	–	–	9.25/14.8	6.1

are accompanied by a fairly low change in the heat capacity of the compound as is often the case for second order transitions. In polarizing microscopy, problems in detection occur when the textures of the neighboring phases differ only slightly or when the textural changes occur slowly. For example, the compound $\bar{8}S5$ has a transition from the smectic-A phase (SmA) to the nematic phase (N) close to the melting point, as well as a supercooled SmA-SmC transition. Both transitions have a fairly low transition enthalpy ΔH (Table 1). The compound TBBA (Table 2) exhibits a supercooled transition of highly ordered smectic phases (SmG-SmH) accompanied by a slow and very decent change in the texture.

RESULTS AND DISCUSSION

The results on $\bar{8}S5$ (Figs 3 and 4) confirm that, depending on the method, some phase transitions are difficult to detect. This finding is especially valid for the DSC-measurements on the SmA-nematic transition in the heating- as well as the SmA-SmC transition in the cooling-cycle. Both transitions are characterized by a very small and rather broad signal (as illustrated in the magnified insertion in Figure 4). The optical measurements on the other hand show an obvious change in the texture accompanied by a significant change in the overall transmission for all transitions. The comparison of the phase transition temperatures derived from the experimental data (Table 1) shows that all methods yield values that are in fairly good agreement with the literature [3], even at the rather high heating and cooling rate of 5 K/min. In most cases the transition appears first in the

TABLE 2 Transition Temperatures and Enthalpies of TBBA, Comparison of the Data Obtained from Optical and Calorimetric Measurements and Literature [3]

Transition	T (°C) Method A	T (°C) Method B	T (°C)/ΔH (kJ/mole) DSC	T (°C)/ΔH (kJ/mole) Literature
Cryst. → SmG	112.11	109.81	111.1/20.23	112.8/19.8
SmG → SmC	141.39	139.78	140.23/4.53	144.0/4.37
SmC → SmA	167.28	166.64	162.56/0.14	172.0/0
SmA → N	197.66	197.66	191.48/0.63	197.7/0.59
N → Iso	233.95	234.05	229.8/1.01	234.0/1.35
Iso → N	233.78	233.79	227.37/0.83	–
N → SmA	202.45	198.60	191.48/0.67	–
SmA → SmC	169.21	169.22	153.71/0.13	–
SmC → SmG	141.35	141.43	135.89/3.32	–
SmG → SmH	85.65	–	82.22/1.08	89.5/1.09
SmH → SmX	72.17	71.67	67.14/0.3	80.0/0.31
SmX → Cryst.	55.66	55.66	55.93/11.96	52

DSC-experiment, i.e., at lower temperatures for the heating and at higher temperatures for the cooling cycle, compared to the optical experiment. This finding can be attributed to the limited thermal conductivity of the glass-covered samples.

TBBA (Figs 5 and 6) exhibits a rich polymorphism in the liquid crystalline state and therefore is a favorite subject for our investigations. In the optical studies of the heating process, the occurring transitions can be easily detected, especially using the differential method (Fig. 5), which yields sharp peaks for all transitions. The integral method B appears to be less significant than method A for the transitions of the ordered smectic phases SmG, SmC and the crystalline state, indicating that the textural changes induced by the respective transitions appear mainly in the grayscale distribution, but less in the overall transmission of the sample. This effect is even more obvious in the cooling experiment. The supercooled phase-transitions SmH-SmX and SmX-Cryst. are very difficult to determine, SmG-SmH appears to be undetectable using the integral method. Nevertheless, the obtained transition temperatures for both optical methods are in fairly good agreement with each other and with literature.

The calorimetric results confirm that the SmC-SmA transition is accompanied by a very small increase in the heat capacity and is therefore difficult to detect. In contrast to the results on $\bar{8}S5$, some of the transition temperatures have a large deviation from those obtained by optical methods and from literature, especially in the cooling experiment. Apart from the fact that all values are lower

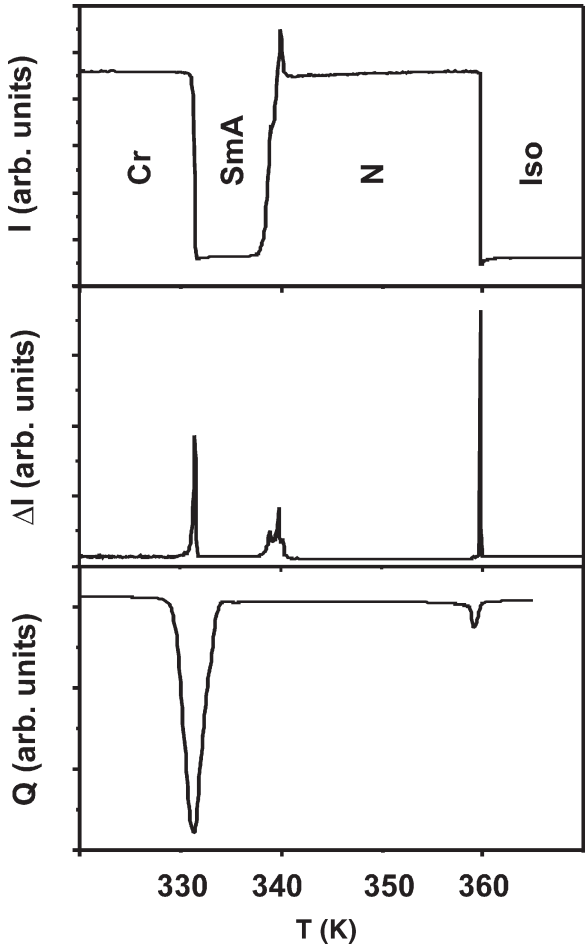


FIGURE 3 Temperature dependence of the integrated light intensity (top), the differential optical signal (center), and the DSC signal (bottom) for $\bar{8}S5$ on heating (5 K/min).

than that in the literature, this appears to be no systematic effect (see Table 2, Cryst.-SmG compared to SmC-SmA), making it difficult to give a simple and satisfying explanation for this finding.

CONCLUSION

In conclusion, we have tested an algorithm (method A) to reduce the data of a video signal efficiently in order to get a scalar function of

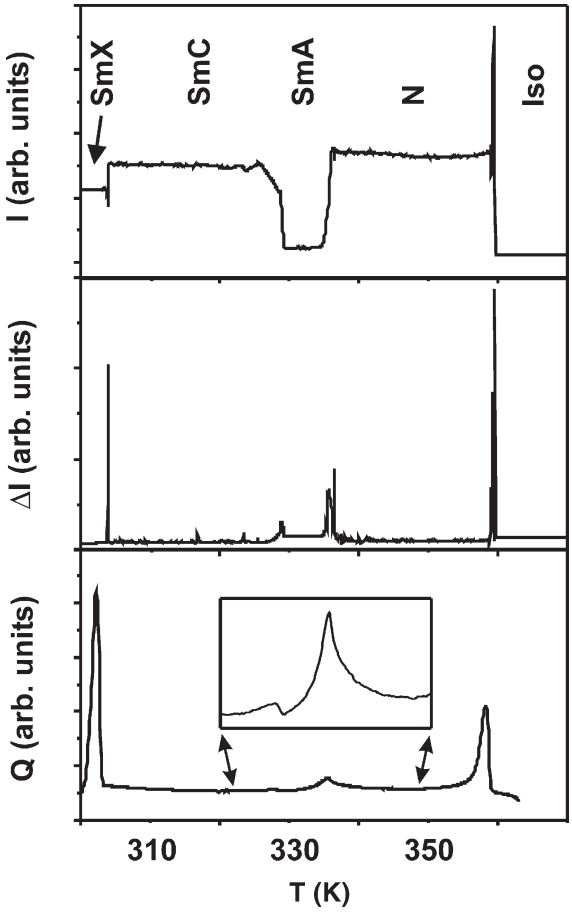


FIGURE 4 Temperature dependence of the integrated light intensity (top), the differential optical signal (center), and the DSC signal (bottom) for $\bar{8}S5$ on cooling (5 K/min). The insertion in the bottom graph gives a magnified view of the marked region.

temperature which indicates the phase transitions. All phase transition in our two model compounds could be detected using this spatially resolved analysis of the signal. The method which we studied for comparison (method B) uses only the integrated brightness of the image and is similar to the signal which we would get from a single photodiode attached to the microscope tube. As expected, this second method has limited capability since it is not suitable to detect all phase transitions in our model compounds accurately.

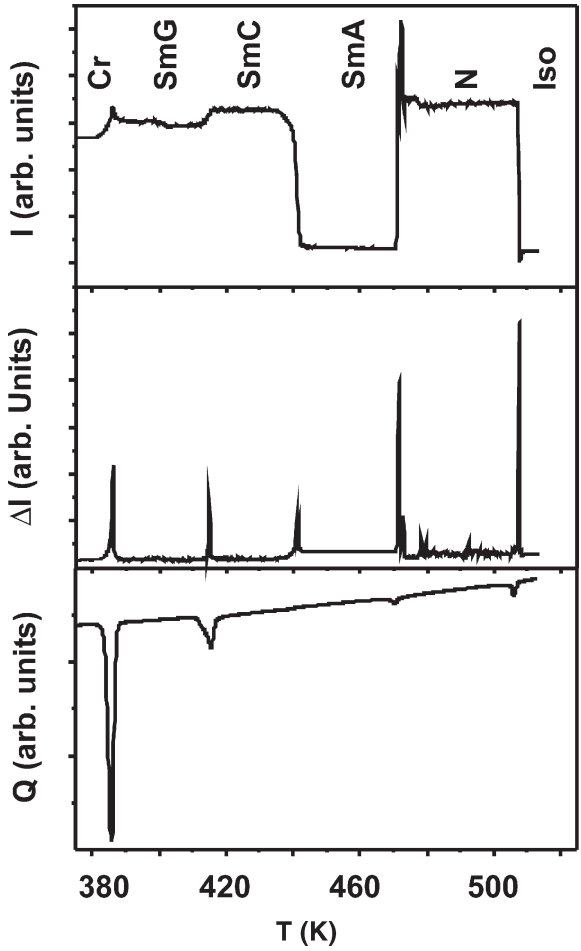


FIGURE 5 Temperature dependence of the integrated light intensity (top), the differential optical signal (center), and the DSC signal (bottom) for TBBA on heating (10 K/min).

A drawback of our favored procedure, the differential method A, is its very high sensitivity which may eventually cause misleading peaks. One of the rare examples are the fluctuations of the signal that can be observed in the nematic range of the heating cycle of Figure 5. While the average permanent fluctuations within the image-frame equal approximately 3 gray levels per pixel with a noise of half a gray-level, these fluctuations are almost twice as high. The local maxima cannot be assigned to any known phase transitions, and

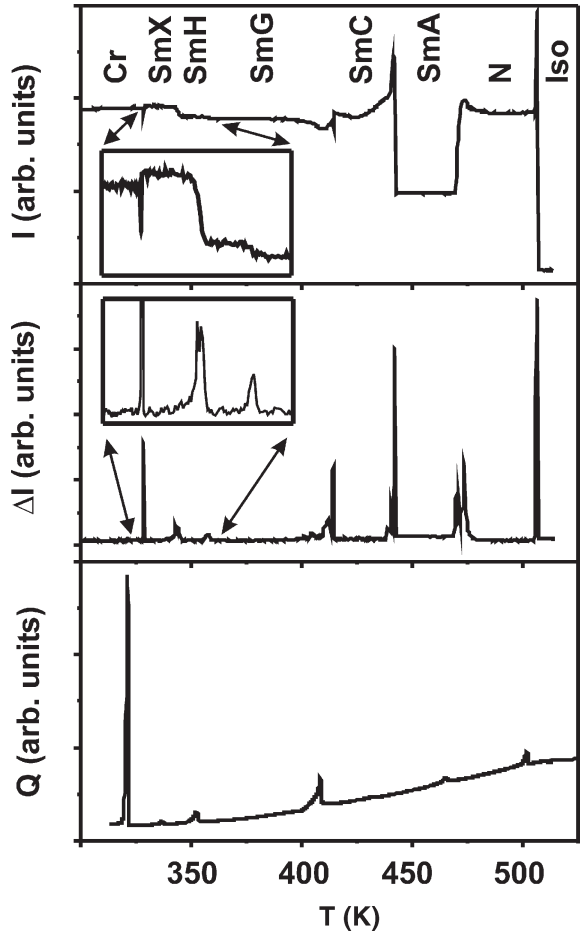


FIGURE 6 Temperature dependence of the integrated light intensity (top), the differential optical signal (center), and the DSC signal (bottom) for TBBA on cooling (10 K/min). The insertions in the top and center graph give magnified views of the respective marked regions.

indeed inspection by eye indicated that these peaks appeared not due to a phase transition but due to flow processes (cover glass floating on the low viscosity material) within the sample. Misleading signals may also be induced by mechanical disturbances of the whole detection system, which result in a small shift of the texture within the microscopic frame. Indeed such artifacts appear preferably in phases with low viscosity (e.g., the nematic phase) or in phases with a fine-grained

texture (e.g., crystalline phases). These effects can be reduced by multiple measurements and mechanical isolation of the experimental setup.

Another artifact is the appearance of multiple peaks sometimes observed in the signal of the differential method (e.g. N-SmA transition in Fig. 4 and Fig. 6). This is due to the fact that the CCD camera performs automatic white-balancing and thus attempts to equalize the overall grayscale of the image, which results in artificial brightening and darkening of some picture areas. The same explanation holds for the overshooting transmission in the integral method, when the texture rapidly changes from a rather dark to a bright state (e.g. isotropic-nematic transition, see Fig. 4 and Fig. 6). This effect however does not dramatically influence the determination of the respective phase-transition-temperatures, as for this purpose the most significant feature of the signal is the onset of the changes, not the shape of the signal.

We conclude that our method is very well suitable for a first characterization of new compounds. The technique can still be improved, for example by color-sensitive detection and real image-analysis with respect to changes of textural characteristics (lines, fans, platelets etc.). Of course, an additional careful identification of the detected phases is necessary in any case.

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