

MODULATED DIFFERENTIAL SCANNING CALORIMETRY

Transitions between monotropic and enantiotropic phases of a cholesteric liquid crystal

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Abstract

The Modulated Differential Calorimetry (MDSC) is applied to the determination of the reversibility in the cholesteryl chloride, which presents a cholesteric monotropic phase between the isotropic and crystalline states. The experimental modulation parameters that govern this method i.e. frequency, amplitude and heating/cooling rate, are determined. MDSC curves and complementary thermomicroscopical observations assign melting, crystallization and liquid cholesteric transition as 'non reversing', and clarification as 'reversing'.

Keywords: cholesteric liquid crystal, Modulated Differential Scanning Calorimetry, monotropic phase

Introduction

The Modulated Differential Scanning Calorimetry (MDSC) [1-3] is stemmed from the combination of Differential Scanning Calorimetry and AC Calorimetry. The principle of this method is first to set the sample under a sine wave modulated heating rate, then to subject the calorimetric response to a mathematical treatment (Fourier transform). The three thermograms obtained represent the 'reversing', 'non reversing' parts of thermal events, and the convolution of both signals, called 'total', which is quite similar to a classical DSC thermogram. It can be proposed for french terminology: *inversible* for 'reversing', *non inversible* for 'non reversing', and *total* for 'total', The 'reversing' part of the calorimetric response shows thermal events that can reverse over the time scale of the oscillation (e.g. heat capacity). The 'non reversing' part shows the component of the response that depends only on time and kinetic processes (e.g. crystallization, cure, ...). The comprehension of 'reversing' and 'non re-

versing' thermal events can then be carried out through the notions of reversible and irreversible processes developed in theoretical thermodynamics.

Previous works performed on polymers [4, 6] have shown that MDSC is a successful technique in deconvolution of superimposed processes e.g. two glass transitions or crystallization and glass transition...; all the studied transformations induce large thermal events. In order to extend the application domain of MDSC, we just have undertaken calorimetric studies of liquid crystal phase transitions. Such compounds exhibit original sequences between stable and/or metastable mesophases; in some cases, transformations occur on small temperature range and with low energy. In fact, most mesophases are enantiotropic, i.e. observable both on heating and cooling a stable or/and a metastable phase. Some mesophases only appear on cooling a metastable phase, and are then called monotropic. The aim of this paper is to bring to the fore the influence of the thermal processing on the reversibility of transitions. Parameters, which govern the deconvolution of the calorimetric response: heating rate, frequency and modulation amplitude, were determined. MDSC curves are discussed and compared with complementary thermo-microscopical measurements.

Experimental

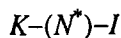
Measurements

The DSC and MDSC measurements were performed on a SEIKO DSC 220C. A liquid nitrogen cooling system allows both cooling and oscillating experiments. The DSC cell was purged with 30 ml min⁻¹ of helium [4]. The MDSC was calibrated for enthalpy and temperature determination with standard indium. All samples were weighted and sealed in hermetic aluminium containers. The reproducibility of temperature and enthalpy measurements were checked on different mass samples, from 3.080 to 9.857 mg.

The thermo-microscopical measurements were performed on an optical polarizing microscope LEICA DMRXP, equipped with a heater/cooler stage CHAIXMECA (93 to 873 K). Samples were prepared both free cell and between slides. Magnifications from 50 to 320 were used.

Material

The cholesteryl chloride (ChCl) was provided by Merck (purity 99.9). It presents a cholesteric (N^*) monotropic phase between the isotropic I and crystalline K states. The phase sequence is described as:



where the brackets mean that the monotropic phase only appears on cooling. This compound has been widely studied, and the thermodynamic data of the literature are reported in Table 1.

Table 1 Thermodynamic data of cholesteryl chloride issued from: literature, classical DSC curves, MDSC ones ('Total', 'Reversing', and 'Non reversing' signals), with: *K*: crystal, *N**: cholesteric, *I*: isotropic liquid, *T_{tr}*: transition temperature (K), ΔH : enthalpy change (J g⁻¹)

	<i>K</i> - <i>I</i>		<i>I</i> - <i>N*</i>		<i>N*</i> - <i>I</i>		<i>I</i> - <i>N*</i>		<i>N*</i> - <i>K</i>	
	<i>T_{tr}</i>	ΔH	<i>T_{tr}</i>	ΔH	<i>T_{tr}</i>	ΔH	<i>T_{tr}</i>	ΔH	<i>T_{tr}</i>	ΔH
Lit. ^[5]	370.0	50.6	-	-	335.0	0.93	-	-	-	-
Classic	366.4	51.7	338.6	-1.4	338.9	1.4	338.6	-1.4	313.4	-35.9
Total	366.2	51.5	338.8	-1.1	339.0	1.0	338.8	-1.1	314.6	-35.5
Rev	"	-0.9	"	~-0.1	"	1.1	"	~0	"	-0.4
Non#rev	"	52.7	"	-1.2	"	~-0.1	"	-1.1	"	-34.5

Modulation parameters

MDSC performances are governed by necessary and sufficient conditions that allow to obtain the more regular sinusoidal temperature modulation as possible. First, the frequency *f* and the heating rate *q* have to be set such that the smaller width for transition temperature range is transversed with no fewer than four or five modulation cycles *n*. Second, for given *f* and *q*, the temperature am-

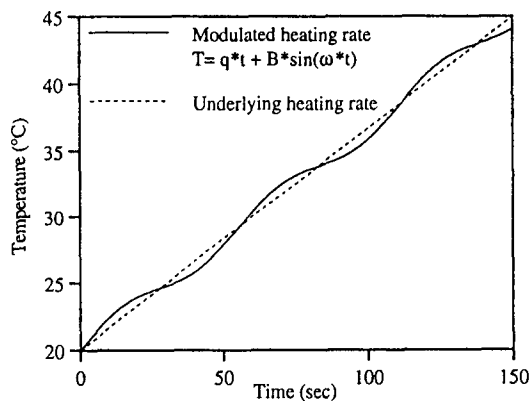


Fig. 1a Modulated DSC curves of cholesteryl chloride; temperature vs. time with $T_{\text{ampl}} = 0.106 \text{ K min}^{-1}$, $f = 0.050 \text{ Hz}$, $q = +2 \text{ K min}^{-1}$ giving an increasing function for the modulated heating rate

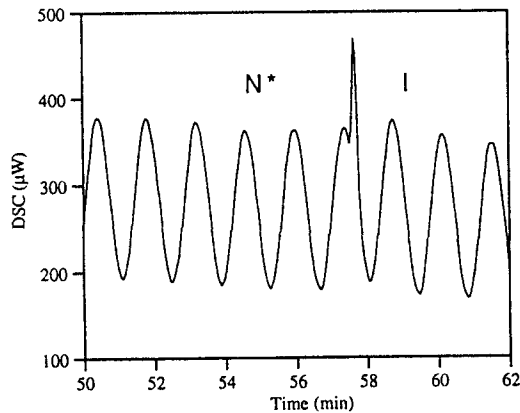


Fig. 1b Modulated DSC curves of cholesteryl chloride; DSC curve for non suitable parameters $T_{\text{ampl}} = 0.443 \text{ K}$, $f = 0.012 \text{ Hz}$, $q = +2 \text{ K min}^{-1}$ and giving insufficient number cycles n through the $N^* - I$ transition

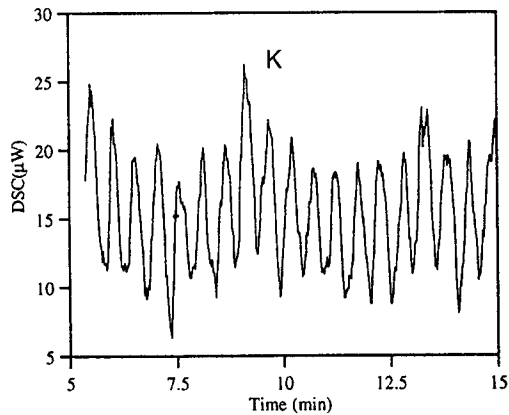


Fig. 1c Modulated DSC curves of cholesteryl chloride; DSC curve for non suitable parameters $T_{\text{ampl}} = 0.013 \text{ K}$, $f = 0.100 \text{ Hz}$, $q = +2 \text{ K min}^{-1}$ and leading to an irregular sine wave modulation in the crystalline phase K

plitude T_{ampl} have to be set such that the modulated heating rate stays an increasing function of time (Fig. 1a); if not, the sample would submit a cooling, which will be characterized, after deconvolution, as 'reversing' and then lead to misconstructions. When short frequencies are used, the transition temperature width could be not large enough to reach the four necessary modulation cycles (Fig. 1b). In opposite, high frequencies allow to increase the modulation cycles and the resolution, but lead to unexploited irregular oscillations (Fig. 1c).

The temperature T is described as:

$$T = qt + T_{\text{ampl}} \sin(2\pi ft),$$

with t as the time. To enhance the oscillation regularity, it must be taken in account that i) decreasing frequency f allows increasing temperature amplitude T_{ampl} , and then increasing sensitivity, ii) slowing heating rate q increases the resolution. As usually for liquid crystal studies, the heating rate q was set equal to $\pm 2 \text{ K min}^{-1}$, because transitions can be assumed as equilibrium processes.

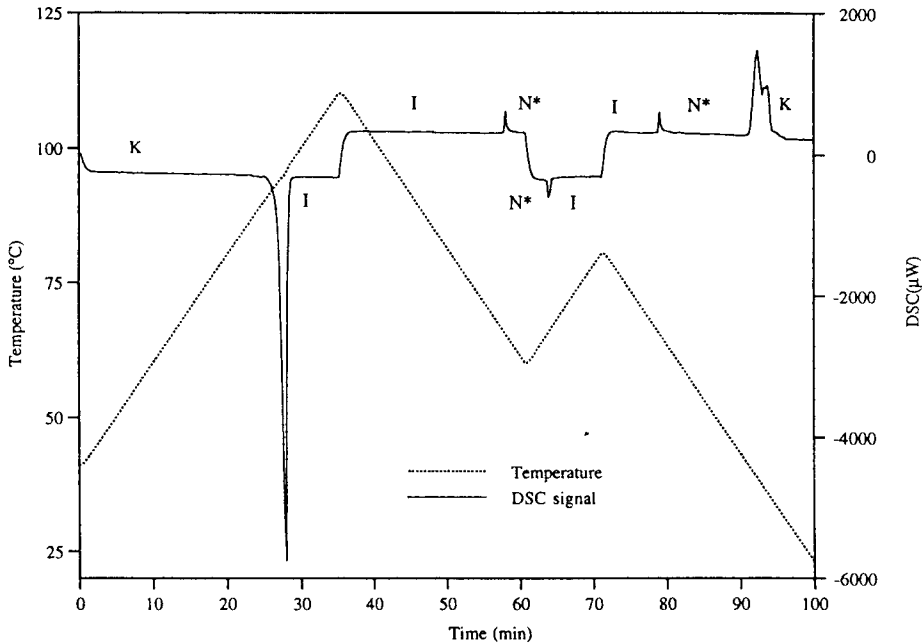


Fig. 2 Classical DSC curve of cholesteryl chloride for $q = \pm 2 \text{ K min}^{-1}$

In order to determine the well fitted experimental parameters, Groves [6] has developed a method especially suitable for energizing thermal events in polymers. It allows to evaluate the modulation parameters from the smaller temperature width of observed transitions for a classical thermogram. Figure 2 shows such DSC curve (full line) of the cholesteryl chloride with heating rates equal to $q = \pm 2 \text{ K min}^{-1}$ (dotted lines). The lower energizing thermal event (N^*-I transition, see below) present the shorter temperature width with $\Delta T = 2 \text{ K}$ or a time period $\Delta t = 60 \text{ s}$. With $n = 4$ (condition on the modulation cycles), the calculated frequency is $f = (\Delta t/n)^{-1} = 0.067 \text{ Hz}$, or a time period $p = 15 \text{ s}$. Following Groves, the amplitude must be set no larger than one fifth ($1/5$) the temperature width, that leads to $T_{\text{ampl}} = 0.4 \text{ K}$ for N^*-I transition. With the selected heating rate $q = \pm 2 \text{ K min}^{-1}$, using both calculated frequency and Groves's conditions the sine wave modulation doesn't lead to an increasing function of time, and Groves's method for parameters determination can't be here applied.

So, we have developed a new strategy more suitable to weak energizing transitions based on the relationship between the amplitude T_{ampl} , the frequency f and the heating rate q . This can be described as [3, 4, 6]:

$$T_{\text{ampl}} = q \cdot (2\pi \cdot f \cdot 60)^{-1}$$

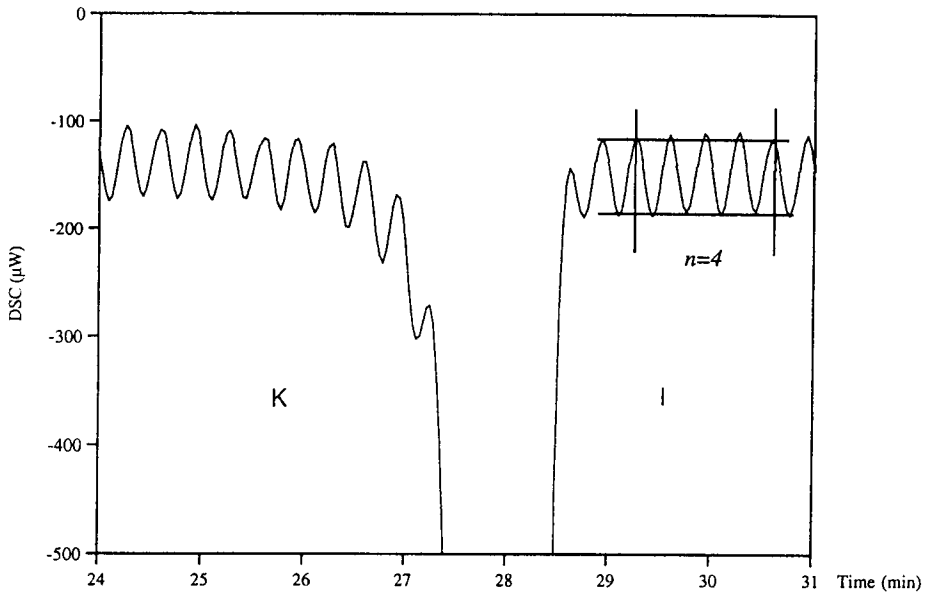
The heating rate was set at $q = \pm 2 \text{ K min}^{-1}$. Different oscillation parameters, resumed in Table 2, were used in order to experimentally determine the optimal conditions of use, i.e. $n = 4-5$, a regular sine wave modulation, and the modulated heating rate as an increasing function of time. The optimal modulation conditions were obtained for an amplitude $T_{\text{ampl}} = 0.106 \text{ K}$, and a frequency $f = 0.050 \text{ Hz}$ (Table 2, col. b). Other parameters lead to irregular modulation (Table 2, col. a) or insufficient cycle number (Table 2, col. c). Figure 3 gives an example of modulated thermograms obtained for ChCl using the three previous parameters. In order to increase the legibility, essential parts of curves were only supplied; Fig. 3 a and b show respectively the $K-I$ transition on heating, and the N^*-I transition on cooling and heating. Remembering first, sensitivity increases in the same way as temperature amplitude T_{ampl} , and second slower heating rate leads to a better resolution, complementary experiments have been performed with $q = \pm 1 \text{ K min}^{-1}$ heating rate; unfortunately optimal modulation conditions were never fulfilled. Slow heating rate and high frequency ($n \geq 4$) involve weaker oscillations, that doesn't lead to a regular sine wave modulation with actual MDSC equipment (Fig. 1c).

Table 2 Experimental modulation parameters T_{ampl}/K : amplitude temperature, f/Hz : frequency, p/s : time period, giving a) irregular modulation, b) ad. oc. modulation, c) insufficient cycle number

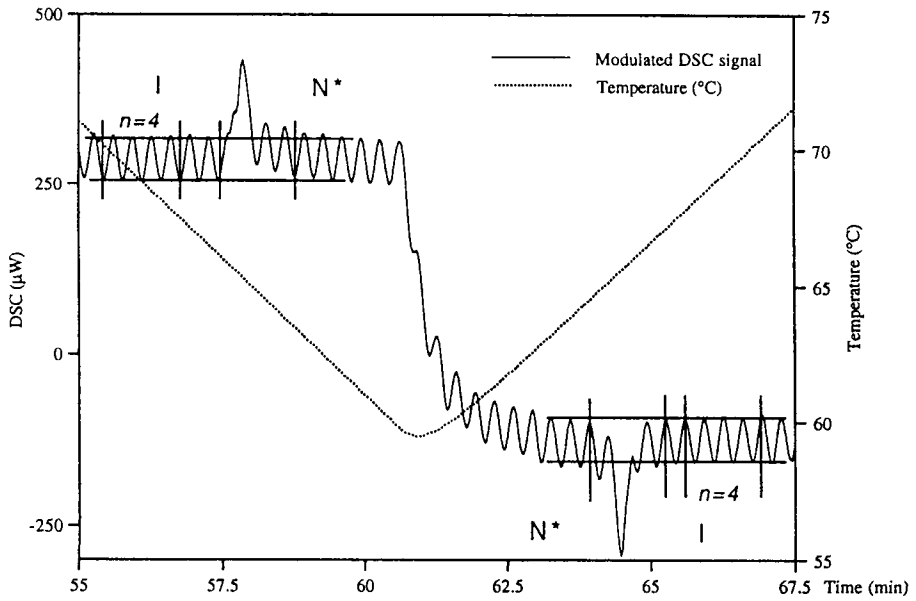
	a		b			c				
T_{ampl}/K	0.053	0.106	0.159	0.212	0.265	0.318	0.372	0.425	0.478	0.531
f/Hz	0.100	0.050	0.033	0.025	0.020	0.017	0.014	0.012	0.011	0.010
p/s	10	20	30	40	50	60	70	80	90	100

DSC curves and optical observations

On classical DSC curves (Fig. 2) the melting $K-I$ is observed for the first heating and the monotropic transition $I-N^*$ is detected for the first cooling. For this last transition, thermodynamic parameters are determined from the second heating scan. Evidently the N^* phase always appears from the I phase at a temperature $T_{I \rightarrow N^*}$ lower than the clarification $T_{N^* \rightarrow I}$, which is the real temperature of the N^*-I equilibrium. When cooling, the N^* cholesteric phase can exist on



(a)



(b)

Fig. 3 Modulated DSC curve of cholesteryl chloride for $T_{\text{amp1}}=0.106 \text{ K min}^{-1}$, $f=0.050 \text{ Hz}$, $q=2 \text{ K min}^{-1}$, a: melting; b: N^*-I transition (cooling/heating).

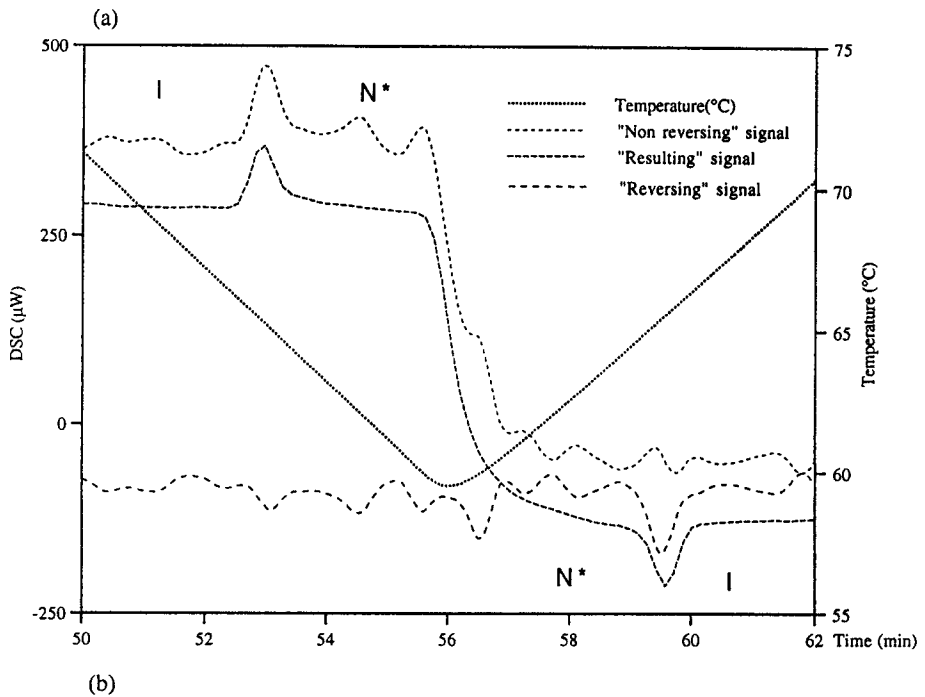
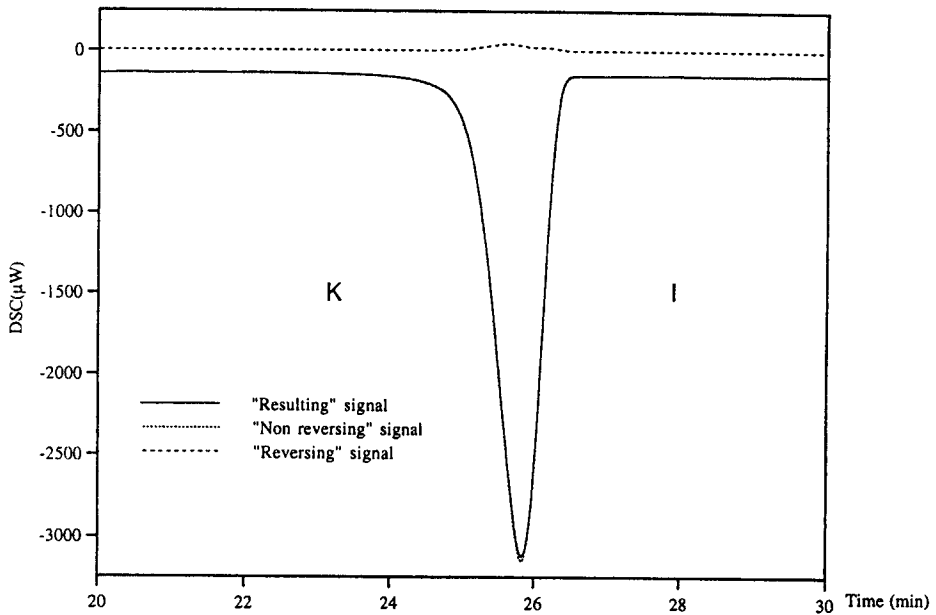


Fig. 4 Deconvoluted thermograms of cholesteryl chloride full line: 'total' signal, dotted line: 'non reversing' signal, dashed line: 'reversing'; a: melting, b: N^* -I transition (cooling/heating)

about twenty degree temperature range before crystallizes. Data issued from Fig. 2 are summarized in Table 1 'classic' line. Enthalpy changes are close to literature data.

Textures and phase sequences obtained from thermo-microscopical studies are presented on Fig. 5. Observations allow to bring to the fore the cholesteric phase undercooles whatever the used cooling rate with $0.1 < q < 2 \text{ K min}^{-1}$.

The MDSC curves has been subjected to deconvolution and treatment. The deconvoluted thermograms of the melting and the monotropic transition (cool-

Photo 1 : Crystal + Liquid for 12 hours
isotherm at 365.9 K

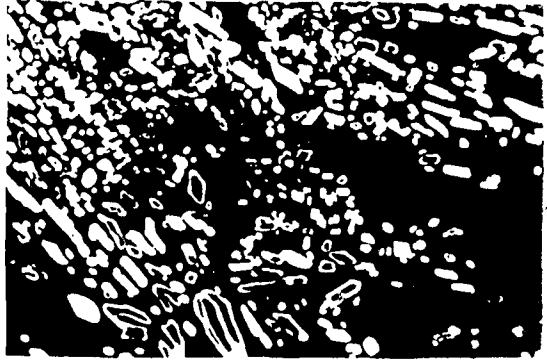


Photo 2 : Crystal texture
at 300 K

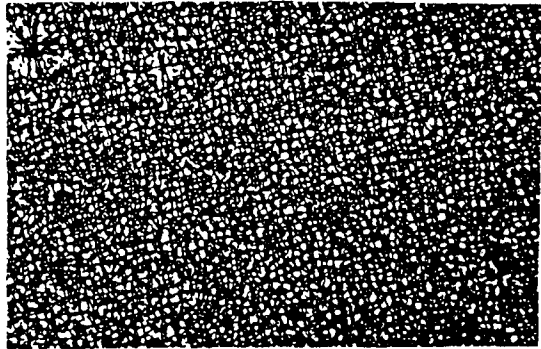
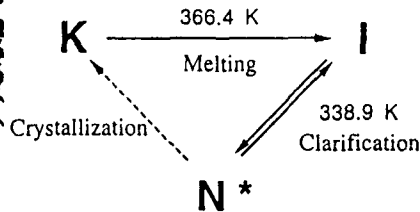


Photo 3 : Cholesteric texture at 325 K

Fig. 5 Textures and phase sequences of cholesteryl chloride.

ing/heating) are presented on Figs 4a and 4b respectively. For both thermal events, the 'total', 'non reversing' and 'reversing' signals are plotted. Temperature and enthalpy changes of transformations are reported in Table 1.

For the melting, both signals 'non reversing' and 'total' are superimposed (Fig. 4a), and the transformation is characterized as a 'non reversing' phenomenon. Therefore growth of crystalline phase *K* from isotropic phase *I* is never possible. In order to check this behaviour, optical observations were performed. A ChCl preparation is heated under the microscope until fifty percent in volume of the sample melts, then cooled and kept twelve hours half degree under the melting point. Then both phases coexist: the birefringent crystalline phase and the 'dark' isotropic liquid (Fig. 5, Photo 1). Despite the long isotherm, no nucleation is observed and crystallites almost don't grow. The weak recrystallization may be associated to the 'reversing' signal observed on Fig. 4a. These optical observations confirm the calorimetric measurements. Quenching under the microscope the half-melted sample at low temperature (260 K) leads to freeze the isotropic liquid: crystallization appears after very long time. Cooling the preparation over a large temperature range (15 K) using slow cooling rates conducts to crystallization. Therefore the *I*-*K* process is clearly governed by time and kinetics. All those results confirm the 'non reversing' character of the crystalline/liquide *K*-*I* transition.

For the *I*-*N*^{*} transition observed on cooling, the 'non reversing' and 'total' signals are clearly separated and the transition is detected as a 'non reversing' phenomenon (Fig. 4b). Thermo-microscopical studies allow to bring to the fore that even using slow cooling rates, the *N*^{*} phase always grows in non equilibrium conditions ($T < T_{N^* \rightarrow I}$) from the undercooled liquid. Optical observations confirm that the *N*^{*}-*I* transition on cooling is characterized as a 'non reversing' phenomenon governed by time and kinetics. It can be noted that *N*^{*} growth appears on a short width temperature range; the four modulation cycles can't be completed and the transition might be also interpreted as 'non reversing'.

On heating the monotropic *N*^{*}-*I* transition is characterized on deconvoluted curves (Fig. 4b) as a 'reversing' phenomenon. Very accurate thermo-microscopical observations performed at $T_{N^* \rightarrow I}$ show the increase and decrease of the *N*^{*} phase vs. the oscillations of the temperature regulation; this confirms that the clarification is an equilibrium transformation.

The crystallization (*N*^{*}→*K*) is characterized by MDSC as a 'non reversing' phenomenon, that confirms crystal growth is a kinetically governed process. Crystallization is always transversed by more than five modulation cycles and then the deconvolution doesn't lead to misconstructions.

Conclusion

The Modulated Differential Scanning Calorimetry was applied to the study of cholesteryl chloride liquid crystal, which presents both enantiotropic and

monotropic phases. A method to determine the experimental modulated parameters is developed especially suitable for weak energizing transitions. The mathematical treatment of the calorimetric signal leads to assign melting, crystallization and liquid-cholesteric transition as 'non reversing', and clarification as 'reversing'.

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