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Optical method for studying phase transitions of thermotropic mesogeneous substances

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A simple analytical system using the light scattering (LS) method has been developed in order to investigate phase transition temperatures of liquid crystals (LC). The changes of the intensity of the transmitted light through a sample were measured as a function of the temperature. All the studied LC showed appreciable changes in the transmitted intensity at the phase transition temperature. The transition temperatures determined by the LS method were identical to those obtained by differential scanning calorimetry (DSC).

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1. Introduction

Some organic substances have a remarkable property: they present certain equilibrium states situated between the crystalline and isotropic liquid phase. These states were named mesophases, or liquid crystal states. Mesophases have peculiar properties, specific both to liquids (not having own shape) and to solid state (anisotropy). At present, under the current conditions of the increasing the number of liquid crystals applications (thermal radiography, detectors and sensors, displays, X – VIS converters), obtaining new substances having such properties, as well as performing new investigation methods of them are important aims.

Differential scanning calorimetry (DSC) and optical microscopy are the most usual methods in liquid crystal analysis. Technological reasons require the use of simple, cheap and satisfactory accurate methods. The study of phase transitions by light scattering (LS) is such a one; the method is based on the measurement of the transmission coefficient of monochromatic radiation as a function of the temperature of the used sample. When a phase transition occurs, transmission coefficient presents a leap.

In this paper we present the study by the LS method of phase transitions for a number of organic substances, comparatively with DSC and optical microscopy methods. Once the agreement with the other methods was proved for some new substances obtained in organic chemistry laboratory of Piteşti University, we used the LS method in order to investigate the influence of the mesogeneous mixture concentration on the transition temperature. We also attempted to perform a phenomenological explanation of the experimental results obtained.

2. Experimental set-up and procedures, used substances

Because of the dependence of light scattering on the wavelength of the used radiation, employing a monochromatic light source is required; solid samples transmittance being very low, the use of a light source having high intensity is also required. Laser is such a light source, as it also has a very good parallelism of the emitted beam. In the experiments we have carried out, a He-Ne laser was used. A photodiode detector receives the light passing through the sample; the signal obtained is amplified and recorded. The temperature of the sample is modified and controlled by a thermostat. The whole process of temperature adjusting and recording the signal produced by the sample is computer controlled [1].

The substances used are presented in Table 1. These compounds were purified and spectrally characterized (IR, RMN techniques) [2]. In our studies, we selected compounds with flexible lateral groups (methylen groups linked with phenyl or cholesteril radicals), knowing that the modifications of the lateral group C-3 sterolic influence physical properties of mesogeneous substances. The main problem in LS method is the change rate of the temperature of the sample. In order to reach the thermodynamic equilibrium of the samples, a very small change rate of the temperature must be ensured [3-5]. The maximum value of temperature change rate of the sample depends on its dimensions and the chemical nature of the substance used. In the case of our experiments, preliminary measurements revealed that a change rate of the temperature of 1^0C in 10 minutes is low enough in order to ensure the thermodynamic equilibrium of the used samples. The diagram of the used experimental set-up is shown in Fig. 1.

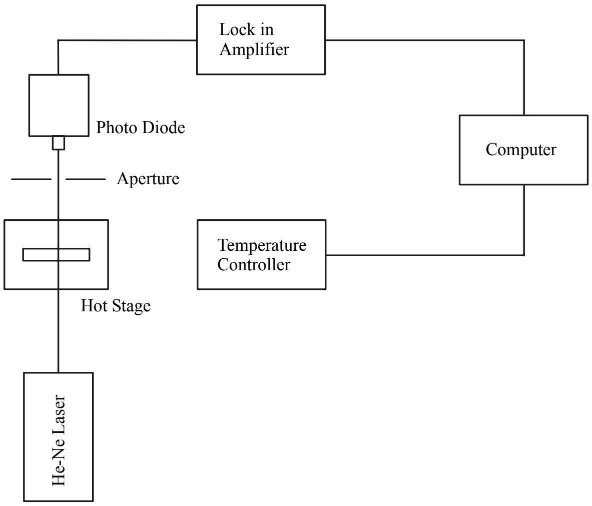


Fig. 1 Block diagram of the experimental set-up used for the study by the LS method of liquid crystals phase transitions.

Thermomicroscopy was performed with polarized light, using a Böetius thermomicroscop equipped with polarizors. By thermomicroscopy, transition temperature and mesophases were determined. Observations were made starting from chamber temperature (crystalline structure) to fusion temperature, both for sterolic compounds and for their mixtures.

The microphotographs for compound **VI** were captured using a JVC TK-C1380 video colour camera with 470 TV line horizontal resolution and 0.95 1x (25%, F1.2) minimum object illumination.

3. Results and discussion

3.1. Dependence of the transmittance of the samples on temperature and chemical structure of compounds

The first group of the experiments we have made followed to verify the possibilities to apply the LC method to certain mesogeneous compounds, as well as comparing the results obtained to those obtained by the POM (polarizing optical microscopy) and DSC (differential scanning calorimetry) methods.

Figs. 2–10 show the results we obtained by the LS method, using the compounds in Table 1. For Figs. 3, 4 and 9, a magnified portion of the graph is attached in the right bootom corner, in order to show the phase transitions.

The main conclusions resulting from these dependencies are the following:

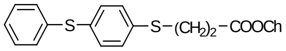
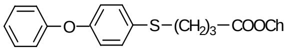
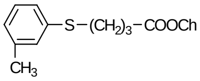
- pure cholesteric mesogeneous compounds present a broad under-cooling interval;
- the transition temperatures have a strong dependence on the chemical structure of the mesogeneous compound, especially on the nature of the terminal radicals;
- in LC state, phenomenon of “transmittance waves” occurs, in the case of all the substances studied. This suggests that the variations of CL transmittance are determined by order changes produced at molecular level.

We could not study the transmittance of **VII** compound, because this presents a strong absorption band in the visible range.

In order to compare the experimental results obtained by the LS method with those obtained by the TM method, we present them in Table 2. The results reveal a good concordance between the methods.

For the first three compounds we made DSC measurements, obtaining LC–isotrope transition temperatures as follows: 47,23 ^{0}C, 81,84 ^{0}C and 78,50 ^{0}C, in good enough concordance with the LS method.

Table 1. Chemical structure of the mesogeneous compounds studied.

Compound	Name of compound	Chemical structure
I	4'-cyano-phenyl-4-hexylbenzoate	$CH_3-(CH_2)_5-C_6H_4-COO-C_6H_4-CN$
II	3(4-diphenylsulphanyl)cholesteryl-thiopropionate	
III	4(4-diphenylether)cholesteryl-thiobutirate	
IV	Cholesteryl-4-*m*-tolylthiobutirate	
V	Cholesteryl-chloroacetate	$Cl-CH_2-COOCh$
VI	Cholesteryl-3-chloropropionate	$Cl-CH_2-CH_2-COOCh$
VII	Sitosteryl-chloroacetate	$Cl-CH_2-COOSit$
VIII	Sitosteryl-3-chloropropionate	$Cl-CH_2-CH_2-COOSit$

where Ch – rest of cholesteryl; Sit – sitosteryl

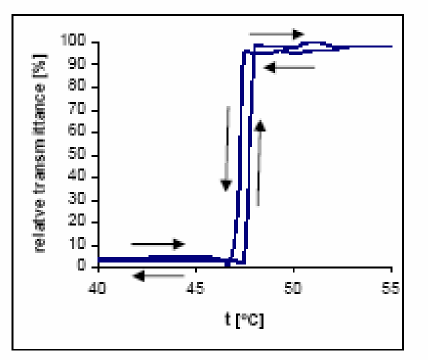


Fig. 2. Dependence of ***I*** *compound transmittance as a function of temperature for heating, respectively cooling.*

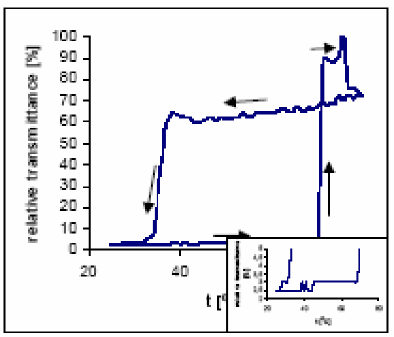


Fig. 4. Dependence of ***III*** *compound transmittance as a function of temperature for heating, respectively cooling.*

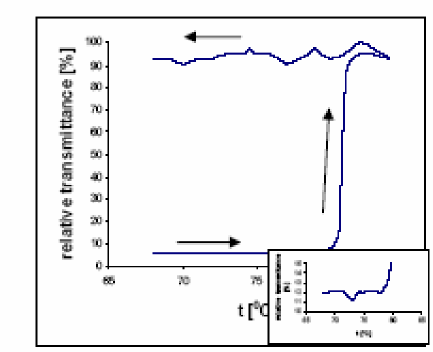


Fig. 3. Dependence of ***II*** *compound transmittance as a function of temperature for heating, respectively cooling.*

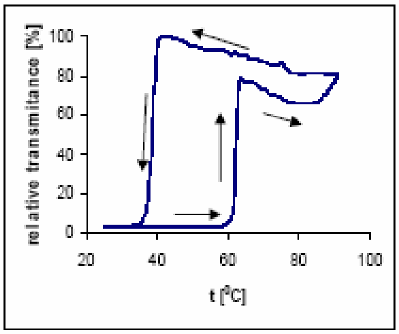


Fig. 5. Dependence of ***IV*** *compound transmittance as a function of temperature for heating, respectively cooling.*

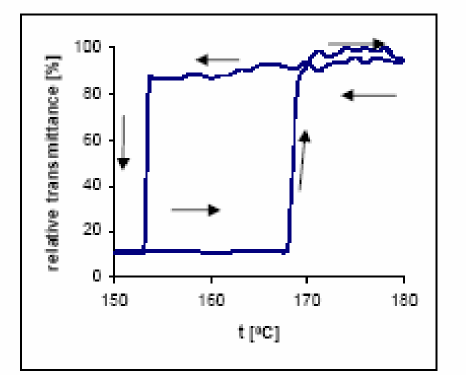


Fig. 6. Dependence of ***V*** *compound transmittance as a function of temperature for heating, respectively cooling.*

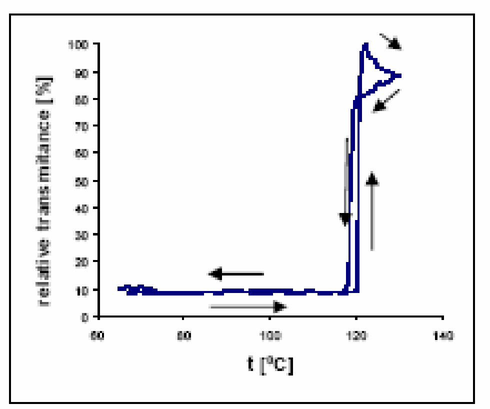


Fig. 7. Dependence of ***VI*** *compound transmittance as a function of temperature for heating, respectively cooling.*

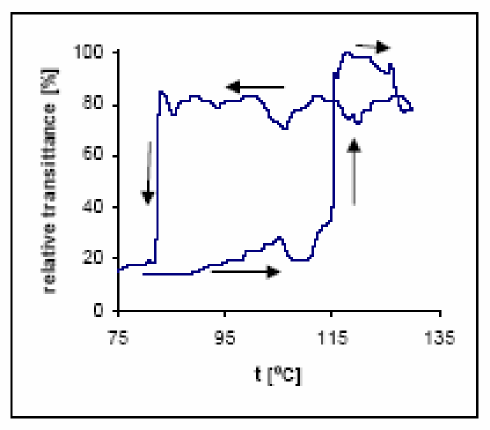


Fig. 8. Dependence of ***VIII*** *compound transmittance as a function of temperature for heating, respectively cooling.*

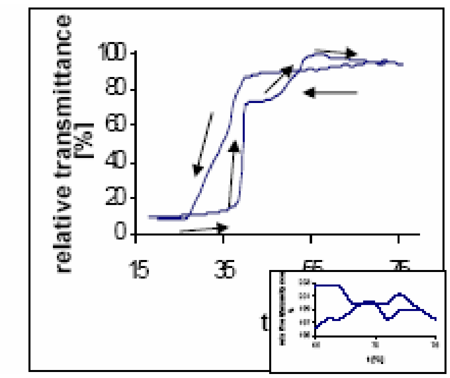


Fig. 9. The dependence of the relative transmittance of ***II*** *–* ***IV*** *(3:1) mixture as a function of the temperature.*

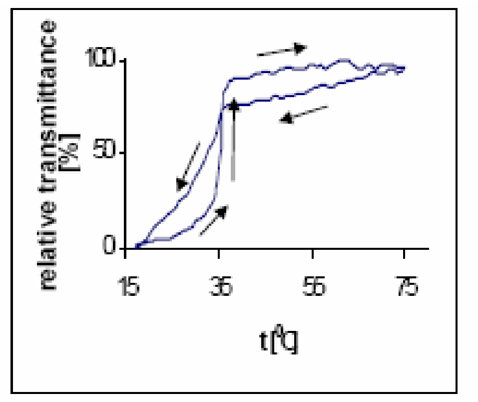


Fig. 10. The dependence of the relative transmittance of ***II*** *–* ***IV*** *(1:1) mixture as a function of the temperature.*

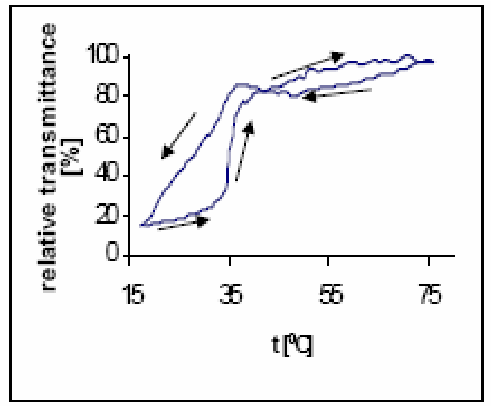


Fig. 11. The dependence of the relative transmittance of ***II*** *-* ***IV*** *(5:7) mixture as a function of the temperature.*

Table 2. Transitions temperatures from LS and optical microscopy data.

Compound	TM t (^{0}C)		LS (temperature at phase transition ^{0}C)	
	heating	cooling	heating	cooling
I	43 shape modification; 46 fusion beginning.	45,5 reorganization begins.	47.5 48	46
II	65 reorganization; 75 fusion beginning.	–	70 73, 78 80.7	-
III	67 blue strains appears; 71 crystals spreading; 74 fusion beginning; 80 start melting	39 reorganization begins.	40 70; 72; 76 80	38-34 32
IV	r.t. white-gray with brown strains crystals; 60 crystal symmetry changes; crystals begin to move; 64 fusion occurs.	47 blue-green circles appear; 42 mosaic of colours (green, red, yellow) appears; 39 polygonal chevron texture; 38 fine chopped texture; 37 mixture of Schlieren and fine chopped textures.	60 64 83 90	75 41 35
V	r.t. white irregular conglomerate; 159-162 fusion	136-135 crystallization in the same shape.	150-160 167 176	153
VI	r.t. white conglomerate overlapped plates; 72 melt with grating appearance; 110 passing to blue colour; 122 colourless melt.	122 crystallization in blue colour begins; 78 passing to yellow-green and crystallization in plates.	70-77; 81 96-104 108; 116 122	120/117 108 79 69-68
VII	r.t. cream-coloured conglomerate; 91-98 crystals displacement; 125 reorganization; 150 yellow melt.	130-120 crystallization in initial shape and colour.	-	-
VIII	r.t. white, acicular, parallel crystals conglomerate; 105-119 colourless melt.	88 acicular, bloom shaped crystallization.	105 110 115-116; 118 120; 129	120 106 85; 83 81

Table 3. Transitions temperatures from LS and optical microscopy data.

Mixtures of compounds	TM t (^{0}C)		LS (mesomorphysm domain, ^{0}C)	
	heating	cooling	heating	cooling
II:IV (3:1)	r.t. irregular structure blue bordered; 50-54 moving; 55 liquid has permanent move: 75-76 melt.	70 blue strain appears.	27; 38.5; 41.47; 55; 75	69
II:IV (1:1)	r.t. fine chopped texture; 45 ordered fine chopped texture; 45-52 continuous moving and symmetry changing of crystals; 72 crystals flow; 87 several crystals become to perspire; 90 melt.	60 crystals radial arranged become to appear; 40 fine chopped texture.	15; 35; 37; 75.5	75; 62; 37.5
II:IV (5:7)	r.t. ordered enough texture; 36 fine chopped texture; 40 continuous moving of crystals; 70 melt.	36 fine chopped texture.	35; 42; 72	42; 34.5; 30; 15

3.2 Experimental study of the transition to liquid crystal of some thermotropic mesogeneous compounds by light scattering method

Practical need of using liquid crystals implies obtaining mesogeneous compounds with a low phase transition to liquid crystal temperature. An efficient method of diminishing this temperature consists in achieving mixtures of mesogeneous compounds with similar molecular structures. Therefore we decided to study, by LS method, the properties of phase transition for two mesogeneous compounds with similar structure, as well as for their mixture. Homogeneous mixtures were obtained weighing the samples (we used the molar ratio 3:1, 1:1 and 5:7 of **II**:**IV**), mechanically mixing and heating them to the fusion temperature. After reverting to the chamber temperature, LS and optical microscopy measurements were made. The results are plotted in Figs. 9-11.

The main conclusions resulting from these dependencies are the following:

Pure cholesteric mesogen presents a large under-cooling interval (about ten Celsius degrees);

LC-ISO and LC-solid (S) phase transitions occur in narrow domains of temperature (comparatively to their under-cooling interval);

Mixtures of cholesteric mesogeneous compounds perform transition LC-ISO at lower temperatures than those of pure compounds (some ten degrees lower);

LC-S transition of cholesteric mesogeneous compounds occurs in a broad interval of temperature (ten degrees);

The domain of LC-S transition is narrow, comparatively with the domain of LC-ISO transition;

In the case of our experiments, the transition LC-ISO for mixtures of cholesteric compounds occurs in the proximity of the temperature of LC-S transition of pure compounds;

Correlating the results of light scattering method with thermomicroscopic observation, we notice very similar transition temperatures (Table 2). Furthermore, by the optical method we can make visual observations on the modification of the specific formations of each mesophase type, produced by the variation of the temperature (form, texture, colour of the crystals).

4. Conclusions

A new optical method for the investigation of phase transitions in thermotropic mesogeneous substances has been devised and tested.

The transiton temperatures determined from this new light scattering method are identical to those obtained from differential scanning calorimetry.

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