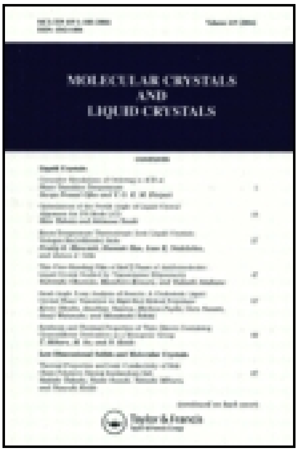

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# The Investigation of the Thermal Stability of Liquid Crystals

Jarosław Szulc [a] & Zofia Stolarz [a]

[a] Military University of Technology, Institute of Chemistry, 01-489, Warsaw, Poland

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# THE INVESTIGATION OF THE THERMAL STABILITY OF LIQUID CRYSTALS

JAROSŁAW SZULC, ZOFIA STOLARZ
Military University of Technology, Institute of Chemistry, 01-489 Warsaw, Poland

Abstract The paper presents the results of the investigation of the thermal stability of compounds being the components of liquid crystal mixtures. For the evaluation of the thermal stability of liquid crystals a modified method was used which consists in exposing the sample to the elevated temperature (150°C) and measuring its resistivity at the same time. It was stated that the thermal stability of a compound is mainly affected by the character of bonds in the molecule and especially by the type of an end group. The most sensitive to the temperature are compounds containing the -NCS group but this cannot be an unconditional proof for the compounds to be chemically unstable at room temperature

## INTRODUCTION

Specific resistivity is an important parameter which decides upon applicability of liquid crystals.[1-7] It is also a sensible parameter allowing for the stability of liquid crystals to be evaluated, because in due course of heating some chemical species which are able to carry out electric current appear. Their concentration is not high and they are difficult to detect using analytical methods but they cause a significant decrease in specific stability of the material and restrict its practical use.

## EXPERIMENT

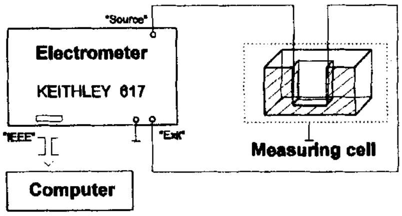


FIGURE 1 The experimental setup

The measurement of resistivity was performed using Keithley 617 programmable electrometer connected to a computer, Figure.1. The measuring cell was a Teflon block with a prismatic cavity inside which there were square platinum electrodes 7 mm x 7 mm, 7 mm apart. The temperature of the cell was controlled using UNIPAN temperature controller type 650H. The cell was inside a Keithley 8002A high resistance test fixture to which, during the whole experiment, dried nitrogen was delivered. The voltage applied to the electrodes was equal to 100 V. The specific resistivity was calculated from the following formula:

$$\rho = R \cdot \frac{S}{l}$$

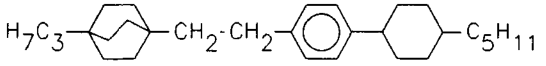
where R- measured resistivity

S -area of the electrodes

l - distance between the electrodes.

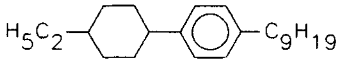
The resistivity of the sample was read and recorded every minute.

The investigated compounds have the following formulas and the phase transition.



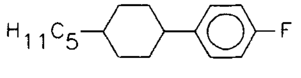
(1)

K 98 $S_B$ 157 N188 I



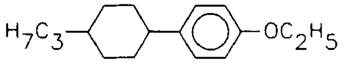
(2)

isotropic liquid



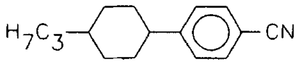
(3)

K 33 I



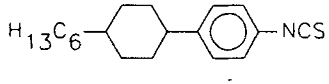
(4)

K 40.7 N (33) I



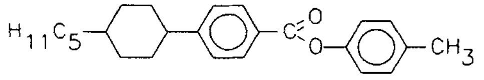
(5)

K 36 N 46



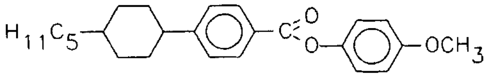
(6)

K 12.5 N 42.5 I



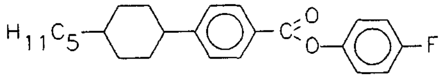
(7)

K 167 N 176 I



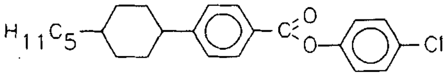
(8)

K 122 N 212



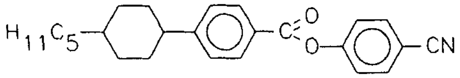
(9)

K 82 $S_B$ 96 N 156 I



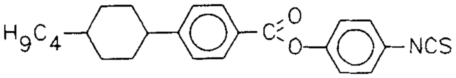
(10)

K 103.5 N 193 I



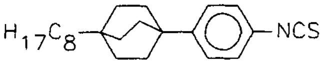
(11)

K 110 N 225 I



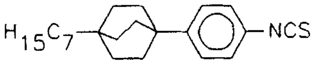
(12)

K 107 S 121 N 230 I



(13)

K 50.5 N 87 I



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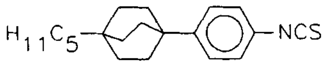
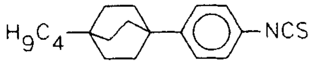
K 56 N 94 I



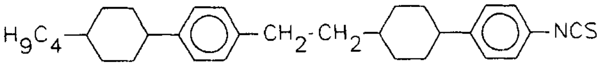
(15)

K 71 N 98 I



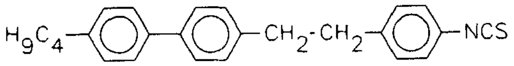
(16)

K 93.5 N (82.5) I



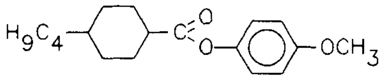
(17)

K 86.5 N 256 I



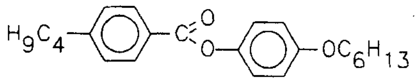
(18)

K 87 N 131 I



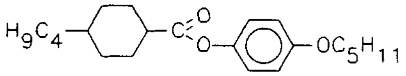
(19)

K 41.5 N 59 I



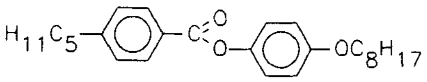
(20)

K 29 N 48.5 I



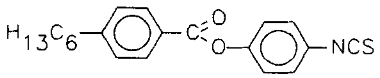
(21)

K 28 N 66.5 I



(22)

K 48 N 62 I



(23)

K 50.5 $S_A$ 49.5 I

All of the compounds were synthesized in the Institute of Chemistry of our University and their purity, checked by gas chromatography, was greater then 99%. Some of the compounds were solids at room temperature so in order to standardize the measurement all of them were dissolved in hydrocarbon 2 (formula 2) which is an isotropic liquid and has very high specific resistivity and high chemical stability.

## RESULTS AND DISCUSSION

The measurement of the resistivity of organic substances using direct current is equivocal to some extend. It results from several factors. First of all after starting of the experiment the readings from the electrometer change in semi exponential way. It is connected with the meter circuit and the changes inside the sample. The charge carriers go from inside of the sample to the electrodes (polarization) and, at least some of them, undergo the electrochemical transformation (electrochemical cleaning)[8].

Before staring the regular testing of the compounds we have checked the measuring method itself. For this purpose a sample containing 10% of compound 1 in hydrocarbon 2 was measured. Before the measurement compound 2 was stored for

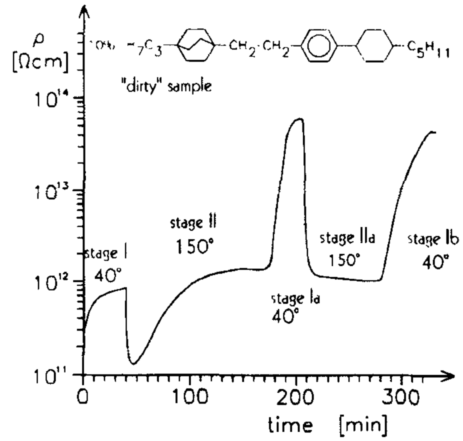


FIGURE 2 Thermostability curve for an impure compound

several days in the humid air. Figure 2 shows the results of the investigation. For 30 min the sample was maintained at 40 °C (stage I) then the temperature was raised to 150 °C and maintained for 2 hours (stage II) whereafter the temperature was decreased do 40 °C (stage Ia) and after several minutes the temperature was returned to 150 °C (stage IIa). After more than one hour the temperature was set again to 40 °C (stage IIb).

The clearly visible increase in the sample resistivity was due in our opinion to electrochemical cleaning of the sample. The sharp decrease of the resistivity at the beginning of stage II is connected with the drop of viscosity as a result of the increase in temperature. After the temperature becomes settled three phenomena occur. One is connected with the generation of charge carriers as a result of the decomposition of sample components. The second is the removal of charge carriers as a result of electrochemical processes going on at the electrodes. The third is the evaporation of traces of water which were embodied in the sample. The third process predominates at first, but at the end of stage II it gives the way to the first one and the resistivity of the sample slowly decreases.

The values of the resistivity at stage I and Ia (the same temperature) differ considerably; the sample contains less water and thus less charge carriers. Repeated heating of the sample causes only the deterioration of the sample resistivity. The generation of the charge carriers dominates over the processes of their removal.

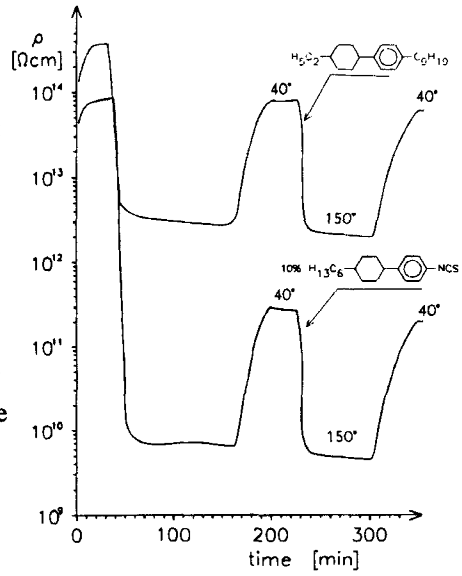


FIGURE 3 Comparison of the thermostability curves for a very stable and less stable compound

Figure 3 shows the change of the

readings while measuring the resistivity of layer of compound 2 and 10% solution of compound 4 in compound 2 for the similar temperature intervals as described above. Hydrocarbon 2 has good initial resistivity and great thermal stability but even in this case the results of keeping hydrocarbon at 150°C are noticeable. The values of the resistivity are not equal to the initial ones when the temperature is returned to 40°C. Slow decrease of the resistivity when sample is kept at the elevated temperature is the evidence of superiority of the processes of the production of charge carriers over the processes of their elimination.

The consideration of the course of the lower curve leads to a conclusion that the worsening of the sample properties takes place during the rise of temperature. When the temperature of 150°C is reached and the sample is kept for same time at this temperature only small increase of sample resistivity is observed. Most damage is done during the first minutes of heating. How long after that the sample is kept at elevated temperature, one or two hours, do not matter for the final value of the sample resistivity. It might suggest that the main assumption justifying the accelerated ageing of the liquid crystal material is not always true. The changes which occur in the sample during short heating do not necessary resemble those which take place when the sample is stored at room temperature.

Temperature influences the rate of any reaction but the temperature coefficient being equal to 2-3 in most cases sometimes can be as high as more than 10 or as low as less than 1.[9] Therefore it is possible that the reaction which are responsible for the ageing of the sample differ from the reactions occurring during the accelerated ageing. In order to conform this assertion the following experiment was performed. The temperature of the sample was increased step by step and the differences between the reciprocal of successive temperatures ( expressed in K) were equal. The changes of the specific resistivity for compounds 2 and 6 are shown in Figure 4.

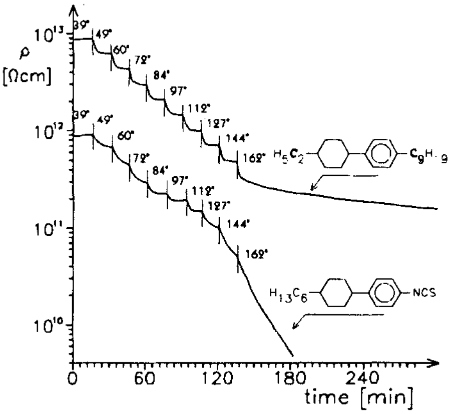


FIGURE 4 The specific resistivity of compounds measured while the temperature was stepwise increased.

On the curve for compound 2 symmetrical steps are seen. This stepwise change of a logarithm of resistivity is connected with the changes of viscosity. The situation in the case of compound 6 is different. The steps are less symmetrical and starting from 127°C the differences between successive values are bigger.

Knowing the restriction of the method we started regular investigation of compounds 3-23. The sample being the 10% solution of an investigated compound in hydrocarbon 2 was placed in a measuring cell and heated to 40°C or 80°C . The initial temperature of the measurement depended upon the solubility of the sample in hydrocarbon 2. The samples during the measurement were single-phase isotropic liquids. The measurement was initiated after the sample reached the initial temperature which was kept for about half an hour. For two successive hours the temperature was equal 150°C and then it was lowered to the initial value. The results presented in the form of a logarithm of the specific resistivity as a function of time are put together in Figures 5-8. In Figures 5,6 and 8 the curve for pure hydrocarbon 2 are shown for comparison. The sharp change of the resistivity noticeable on these figures results from the sharp change of the sample temperature; from 40°C (80°C) to 150°C and from 150°C to 40°C (80°C).

Figure 5 shows the measuring curves for cyclohexylbenzene derivatives (compounds 3-6) which differ in the terminal groups. The molecules of all these compounds have the same skeleton as hydrocarbon 2. Compound 6 containing the -NCS group is the least stable. The specific resistivity of this compound after the accelerated ageing diminishes thousand times. Compound 5 containing the -CN group do not change its resistivity so severely as compound with the -NCS group but it is not the evidence of its high stability. The initial resistivity of compound is relatively small. The more polar a compound is the more difficult it is to free it from impurities conducting the electric current. Compound 3 with fluorine and compound 2 with an etoxy group have rather high stability.

The measuring curves for phenyl alkycyclohexylbenzoesates which differ in the substituent in the phenyl moiety are given in Figure 5. The initial temperature for all these compounds was 80°C. Comparing the curves in Figure 5 and in Figure 6 one can conclude, that the character of the terminal group is a decisive factor for the preservation of the thermal stability. The presence of the bridge group -COO- has almost no impact on the course of the measuring curves. The same conclusion can be drown out from the analysis of the curves in Figure 7.

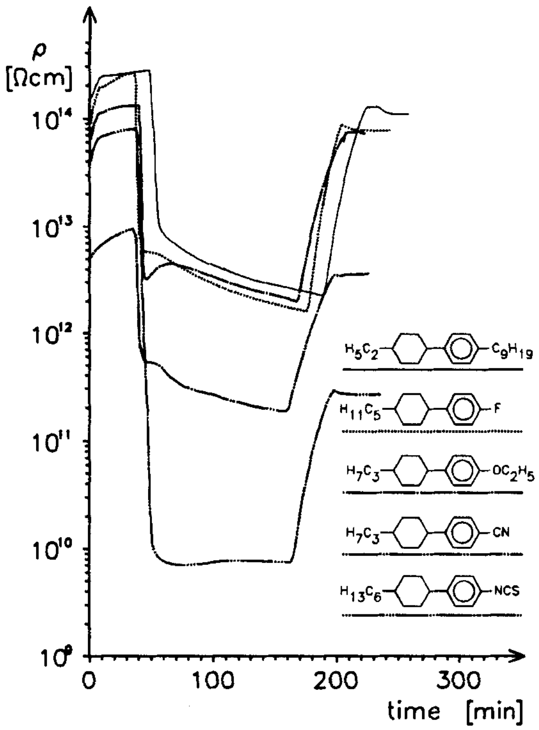


FIGURE 5 Thermostability curves for compounds with different end groups

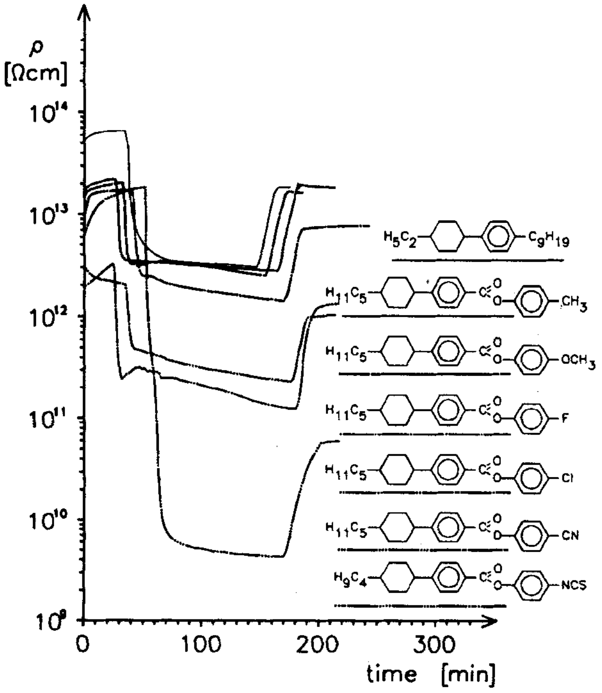


FIGURE 6 Thermostability curves for esters

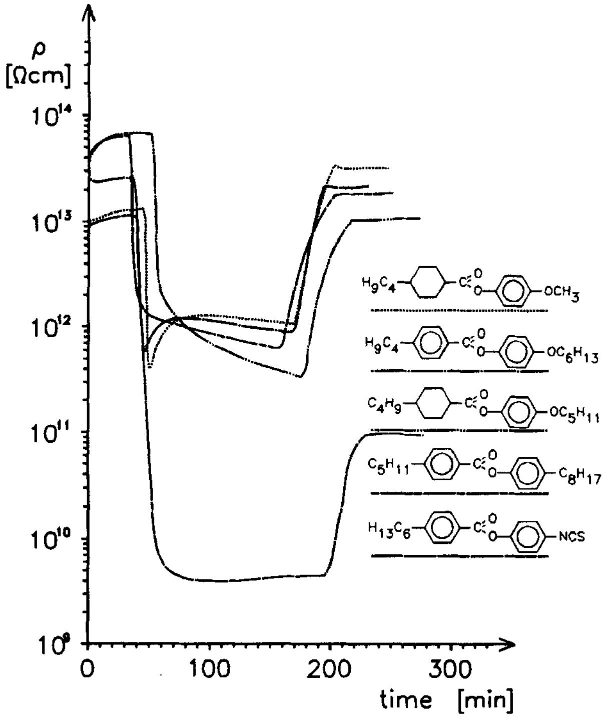


FIGURE 7 Thermostability curves for "short" esters

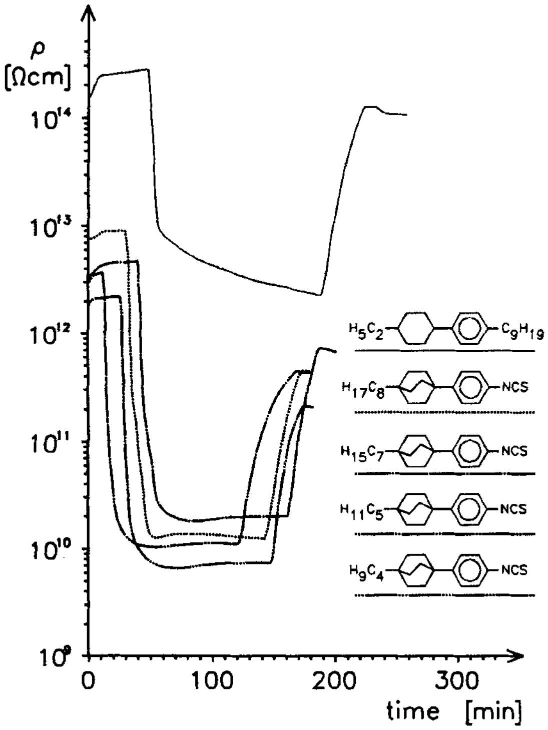


FIGURE 8 Thremostability curves for derivatives of bicyclooctane with -NCS group

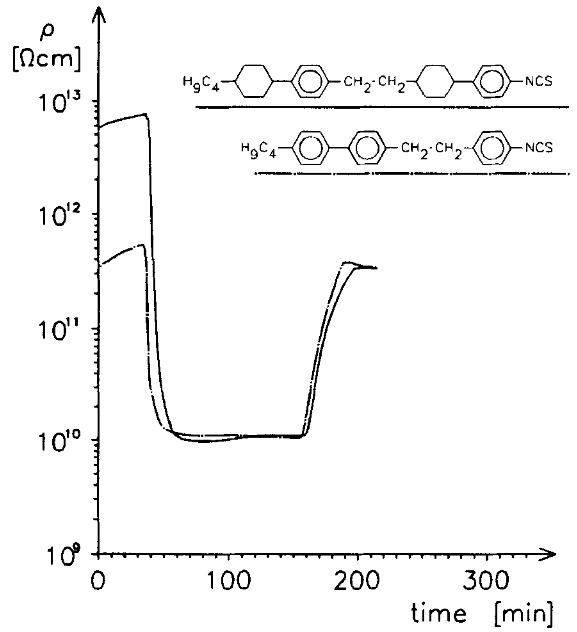


FIGURE 9 Therostability curves for compounds with different initial specific resistivity

The changes of the specific resistivity for alkylbicycloisothiocyanatobenzenes are shown in Figure 8. These compounds have different alkyl chain lengths but it should not influence the resistivity therefore the differences in the route of the curves can only by justified as being the results of differences in the way the compounds were obtained and purified. The reproducibility of the measurement is also noticeable here.

The comparison of the curves in Figure 9 allows to conclude that the ratio of the specific resistivity before and after the accelerated ageing can not be the measure of sample stability. For compounds 17 and 18 this ratio is different but the thermal stability is similar. In the case of compound 18 the increase of the number of charge carriers is difficult to notice because they are in the sample before the aging process.

## CONCLUSION

The method which was used for the evaluation of the thermal stability gives good results on the condition that the initial specific resistivity of the compounds is very high. It allows to estimate the initial purity of the liquid crystal and its chemical stability.

The thermal stability of a compound is mainly affected by the character of bonds in the molecule and especially the type of an end group. The most sensitive to the temperature are compounds containing the -NCS group but this cannot be an unconditional proof for the compounds to be chemically unstable at room temperature

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