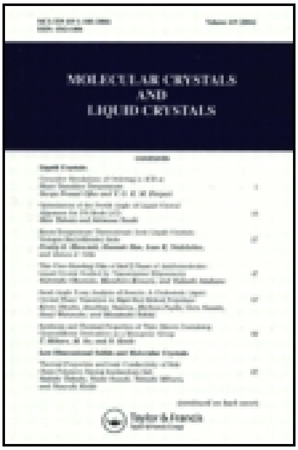

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Spectroscopy Investigation of Ferroelectric Liquid Crystals Composed of Banana-Shaped Achiral Molecules

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Banana-shaped liquid crystal called F-490 composed of achiral molecules has been examined by means of polarizing microscopy, differential scanning calorimetry (DSC) as well as optical (visible and UV) and dielectric spectroscopy methods. The results show phase diagram of this compound. It forms monotropic liquid crystal phase called B_2 which is antiferroelectric. Moreover the formation of solid phase depends upon thermal history.

Keywords: banana-shaped molecules; B_2 phase; dielectric spectroscopy; DSC calorimetry; polarizing microscope observation; visible and ultraviolet absorption spectroscopy

INTRODUCTION

In recent years in the field of liquid crystal research a new sub field is emerging. Besides the normal rod-like and disc shaped molecules new class of compounds was synthesized, banana-shaped ones [1].

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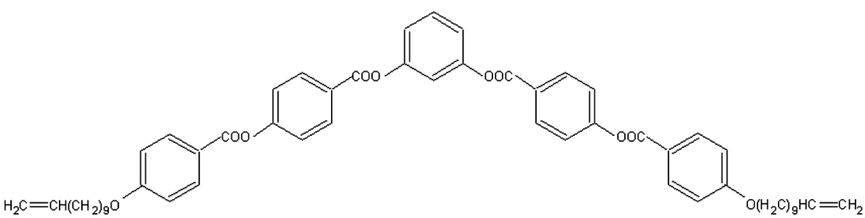
Generally they consist more than three phenyl rings (usually odd number of rings) linked *via* non-linear linking groups such as carboxy-, azomethine or other which kink the shape of molecule. The first banana-shaped compounds were presented in 1996 by Niori *et al*. [2] soon followed by other groups (e.g., [3]). It was discovered these compounds form new mostly two-dimensional structures different than normal smectic phases, called according to Berlin convention B_1–B_7. The assignment of these new structures is based mainly on measurements of X-ray diffraction but also on other complementary studies like optical, dielectric, electrooptical or NMR spectroscopy.

The aim of the studies presented here was to observe newly synthesized banana-shaped molecules in order to check ferroelectric character of the phases being formed as well as to control the phase diagram.

EXPERIMENT

Banana-shaped liquid crystal compound



called for simplicity F-490 synthesized at Research Institute for Solid State Physics and Optics of the Hungarian Academy of Sciences composed of achiral molecules has been examined by means of several spectrosco-optical methods. Initial identification of mesophases has been done by investigating the substance using polarizing microscope (Biolar PI equipped with Linkam hot-stage THM600 and temperature controller TMS90. Data were registered with CCD camera and VHS system – some results were digitized and stored in computer). Several series of measurements with different rates of heating and cooling (in the range from 1 to 30 degrees per minute) have been performed. Apart from melting point and clearing point we observed change of the texture at 69°C during heating.

Also other experiments were carried out in the same manner. The differential scanning calorimetry (DSC) measurements were performed using Perkin-Elmer DSC7 setup with liquid nitrogen cooling device.

Dielectric studies have been done with HP set-up at frequency 0.440 kHz using LINKAM 5 μm cells and dielectric dispersion as well as absorption were calculated from the data. Also the triangular voltage wave was applied to observe the ferroelectric like switching in achiral system. To this end a reversal current method using a digital HP scope with IEEE-488.2 interface driven by a Scope Link Program has been used. Absorption spectra in the visible and UV range were measured using Ocean Optics Inc. spectrometer with Basic Acquisition Software.

RESULTS AND DISCUSSION

The Figures 1 and 2 present the results of our DSC studies with different heating and cooling rates. It is shown here that the heating results are rate independent, always exhibiting only one phase transition, namely melting from crystal to isotropic liquid at 361 K, whereas the rate of cooling procedures strongly influences the observed results. One can notice monotropic sequence of transitions. The first transition

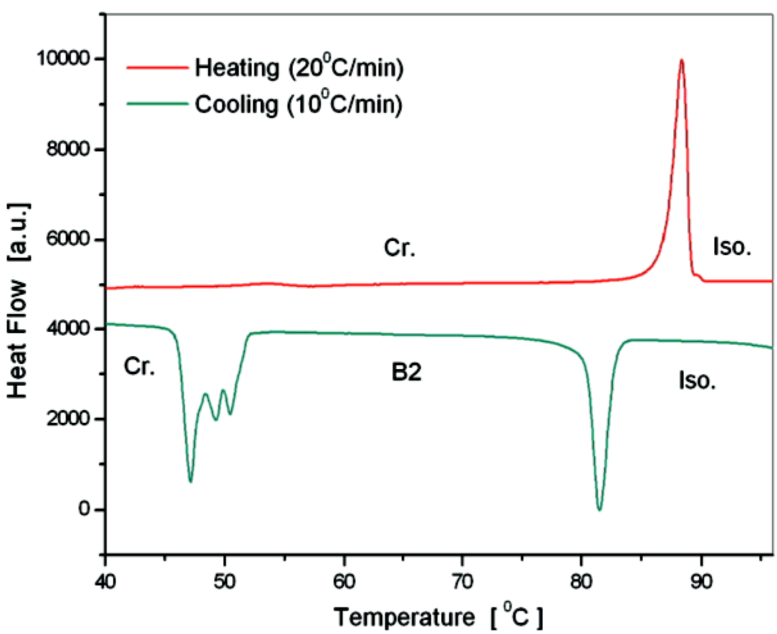


FIGURE 1 DSC calorimetry results (heating rate - 20 deg/min, cooling rate - 10 deg/min).

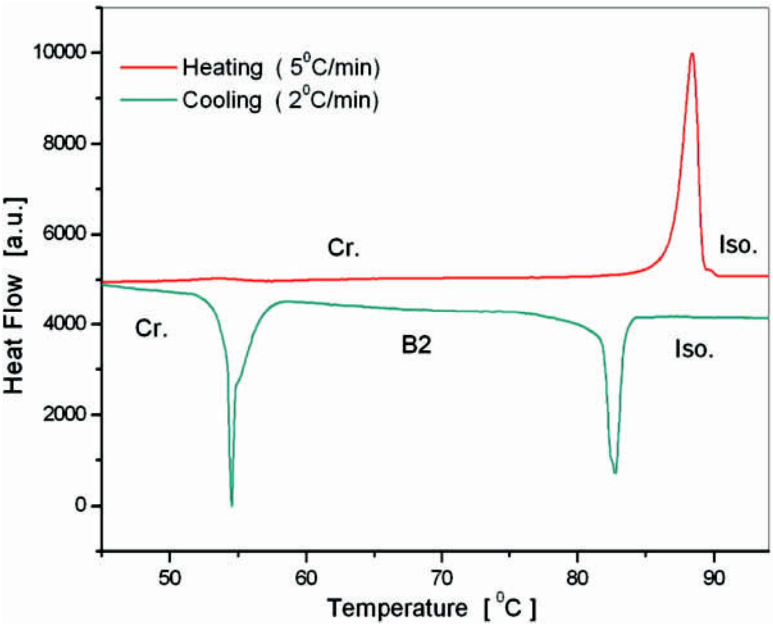


FIGURE 2 DSC calorimetry results for lower heating and cooling rates (heating rate - 5 deg/min, cooling rate - 2 deg/min).

is observed at the temperature slightly lower than melting (355 K). Then upon further cooling another phase transition is observed as the single one with some preparatory effects at 327 K when cooling is moderate (2 deg/min) but when the cooling was rapid (10 deg/min or faster) the phase transition appears at lower temperature, below 323 K (what was expected as normal undercooling effect) and is split to several non completed transitions (in Fig. 1 there are three not separated observed). When the transitions would be completed then the respective DSC peaks would reach their base in each time not only after the last one.

The character of the phase transitions was checked with the polarizing microscope, proving the melting to isotropic non optically active phase on heating as well as the liquid crystalline phase observed on cooling below the clearing point. The results observed on cooling are shown in Figures 3 and 4. The comparison with the textures observed in other banana-shaped molecules suggest the designation of B_2 phase for this one shown in Figure 3 [4], whereas the growth of nuclei shown in Figure 4 confirms the crystallization as the transition observed at the range of 320 K. Probably at more rapid cooling

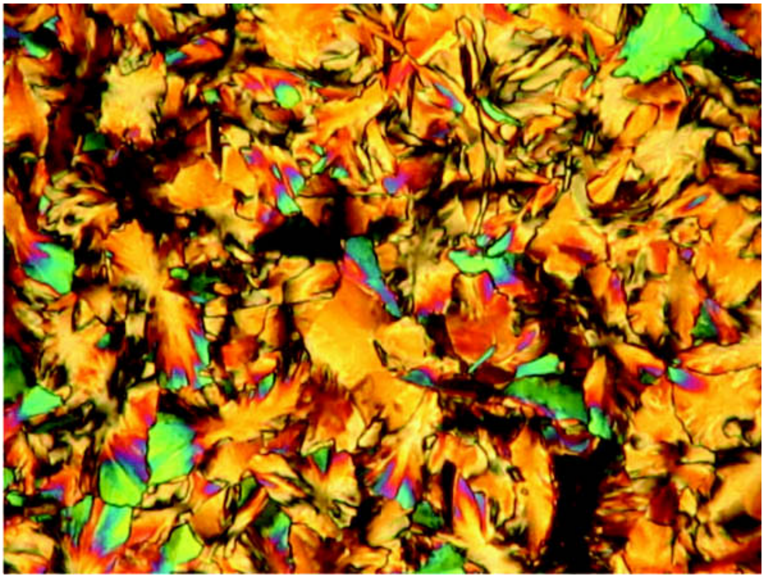


FIGURE 3 Texture of mesophase observed on cooling using polarizing microscope (B_2 like texture).

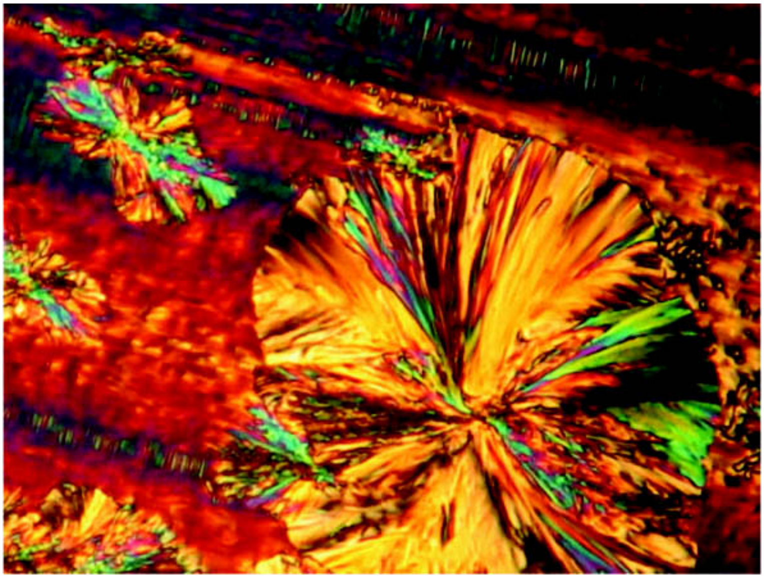


FIGURE 4 Texture of mesophase observed on cooling using polarizing microscope (growth of solid phase nuclei).

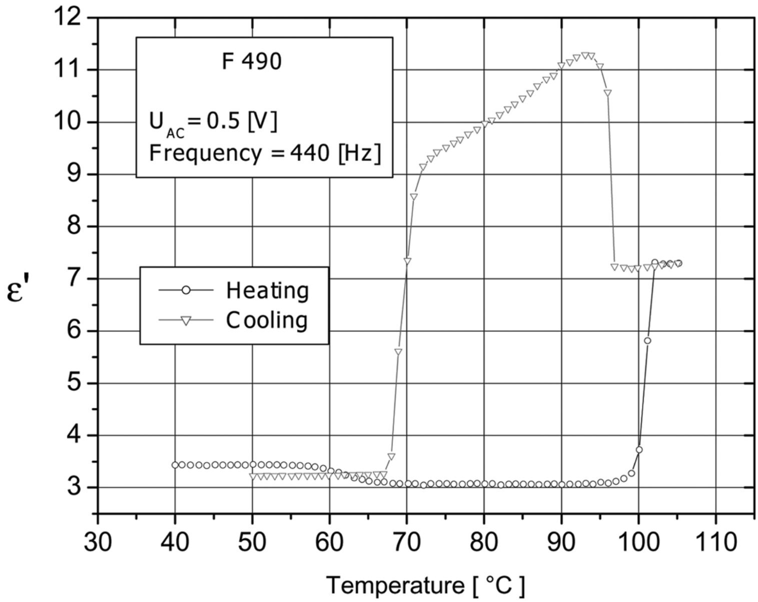


FIGURE 5 Results of the temperature variation of the dielectric dispersion on heating and on cooling.

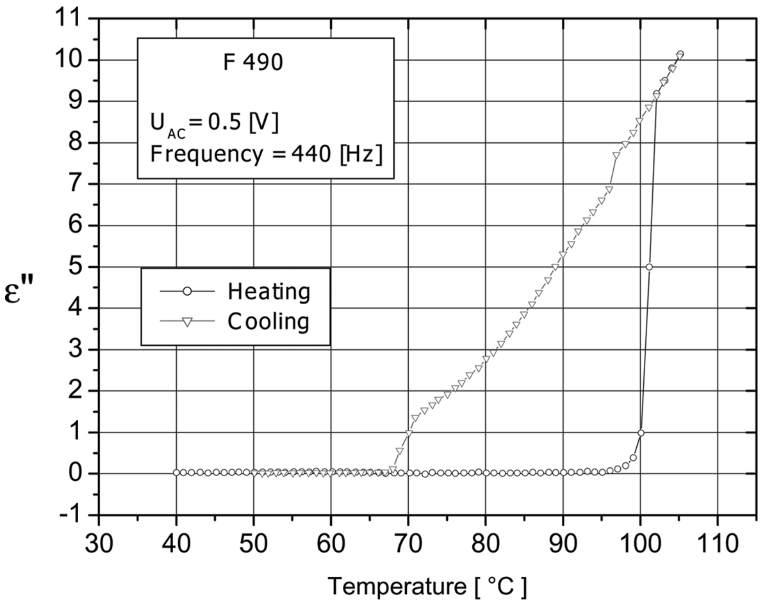


FIGURE 6 Results of the temperature variation of the dielectric absorption on heating and on cooling.

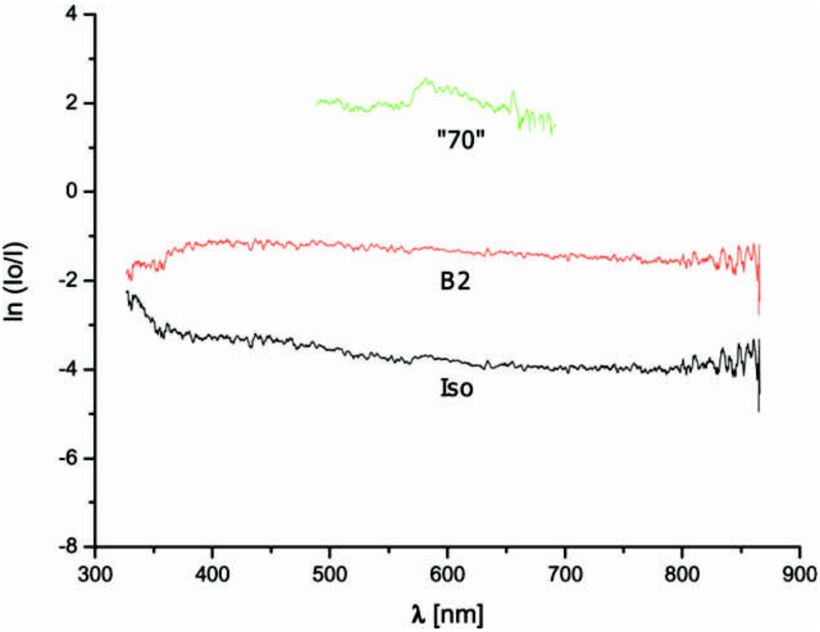


FIGURE 7 The results of reflectance measurements of visible and UV light.

the nucleation process was not completed and therefore the observed transition is the mixture of nucleation and propagation of crystal phase. The flexible structure of the molecules facilitate such processes.

Figures 5 and 6 present the results of dielectric studies, namely temperature variation of dielectric dispersion on heating and on cooling (Fig. 5) as well as dielectric absorption results in both cases (Fig. 6). The dielectric dispersion curve (Fig. 5) reveals the existence of a step (a decrease) of ε' (the dielectric constant) for the first run on heating at 69°C. Because investigated sample appears only melting transition on heating the change of ε' can be interpreted as "crystal to crystal" transition likely due to the fact that the dielectric permittivity is a tensor quantity. For liquid crystalline systems the principal components of the dielectric permittivity tensor show different temperature dependencies and contributions to the dielectric spectrum as connected with the varying position of the permittivity ellipsoid. So we would like to suggest that the change in the dielectric effect at 69°C is due to the reorientation of the permittivity ellipsoid.

The results of reflectance measurements of visible and UV light are shown in Figure 7. Due to the strong coupling of π electrons of liquid

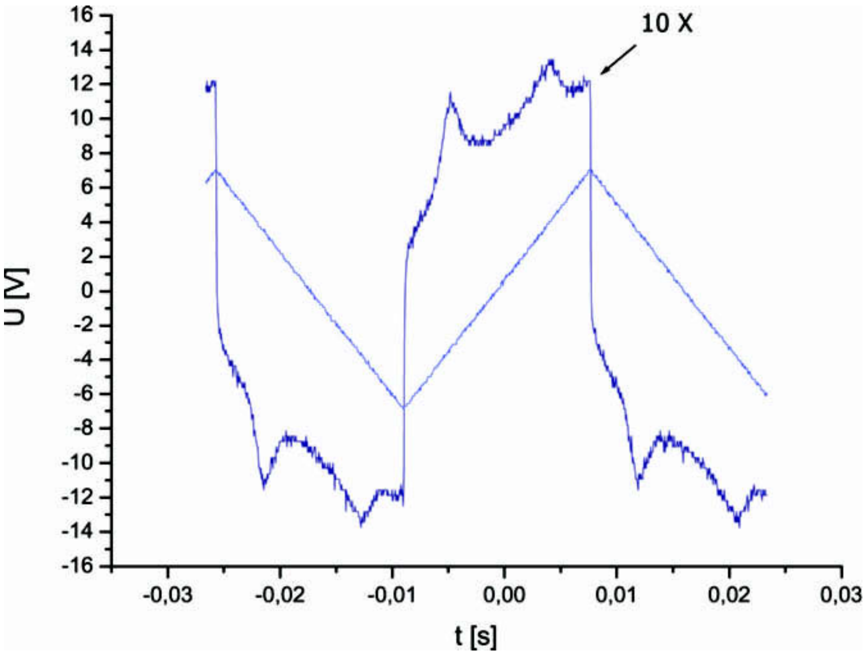


FIGURE 8 The reversal current results as registered after applying triangular voltage wave.

crystal molecules the observation of visible and UV spectra is useful method to study such systems. In our experiments we have proved that at 69°C there was clear change of measured spectrum. It corresponds to step of the dielectric permittivity observed in dielectric studies.

Moreover during the dielectric spectroscopy investigations the possible ferroelectric properties of B_2 phase were checked. The reversal current was registered after applying triangular voltage wave. This effect was observed and results are shown in Figure 8. Analyzing it one can conclude the B_2 structure in F490 molecule is the antiferroelectric phase because of two components of spontaneous polarization that were observed.

CONCLUSION

The newly synthesized banana-shaped molecule named in short F490 forms liquid crystalline structure B_2 in monotropic way (on cooling). This phase is antiferroelectric one. The cooling rate influences solidification process and the properties shown on cooling strongly depend upon thermal history of the sample. Some results suggest also interesting features at the temperature 69°C.

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