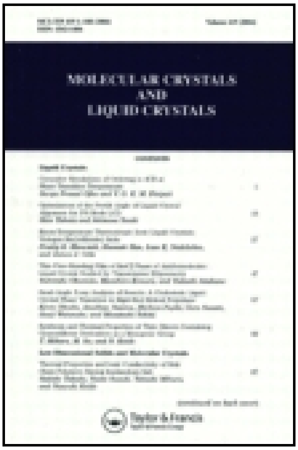

Molecular Crystals and Liquid Crystals

Dielectric and XRD Investigation of Ferroelectric Liquid Crystal Composed of Banana-Shaped Achiral Molecules

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Dielectric and XRD Investigation of Ferroelectric Liquid Crystal Composed of Banana-Shaped Achiral Molecules

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An achiral banana-shaped called F-490 liquid crystal has been examined by means of polarizing microscopy, differential scanning calorimetry (DSC) as well as X-ray diffraction (XRD) and dielectric spectroscopy methods. The phase diagram of the compound is proposed. The F-490 forms crystal-like phases the B_4 and the B_3 on heating and the banana-like antiferroelectric phase B_2 as well the B_3 and the B_4 phases on cooling. Moreover, the formation of solid phase depends upon thermal history. Dielectric studies have been done with HP set-up in a wide frequency range of 0.01–1.5 MHz using LINKAM 5 μm cells. Dielectric dispersion as well as absorption were calculated from the data. On the base these data the complex rotational dynamics of banana-shaped molecule have been described. The layer thickness and the unit cell parameters of B-phases were determined on the base of XRD results.

Keywords: banana-shaped molecules; B_i phases; dielectric spectroscopy; X-ray diffraction

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 bent-core compounds was synthesized, banana-shaped ones [1]. Generally they consist more than three phenyl rings (usually odd number of rings) linked *via* non-linear linking groups such as

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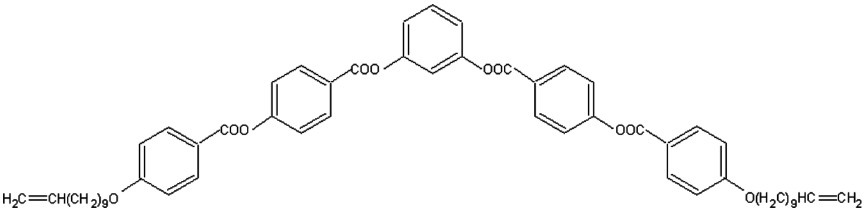
carboxy-, azomethine or other which kink the shape of molecule. The first banana-shaped compounds were presented in 1996 by Niori *et al.* [2] soon followed by other groups (e.g., [3]). It was discovered these compounds form new mostly two-dimensional structures different than normal smectic phases, called according to Berlin convention B_1–B_7. Now, the new structure designated as B_8 has been reported [4]. The assignment of these new structures is based mainly on X-ray diffraction measurements 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 molecular dynamics 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 was examined by means of several spectrosco-optical methods. The initial identification of mesophases was done by investigating of the substance using the 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) were performed. Apart from melting point and clearing point we observed change of the texture during heating. Also other experiments were carried out in the same manner. The differential scanning calorimetry (DSC) measurements were performed using the Perkin-Elmer DSC7 setup with liquid nitrogen cooling device. The Low Frequency Dielectric Spectroscopy diagram was used as a classical thermogram. Dielectric studies were done with HP set-up at frequency 0.440 kHz using LINKAM 5 μm cells.

On the base of XRD, DS and DSC technique results we propose for F-490 the following diagram:

- on heating:

$$\mathrm{Cr} \xrightarrow{\approx(-70^\circ\mathrm{C})} \mathrm{B}_4 \xrightarrow{=(+54^\circ\mathrm{C})} \mathrm{B}_3 \xrightarrow{=(+88^\circ\mathrm{C})} \mathrm{l}$$

- on cooling:

$$\mathrm{l} \xrightarrow{=(+82^\circ\mathrm{C})} \mathrm{B}_2 \xrightarrow{=(+52^\circ\mathrm{C})} \mathrm{B}_3 \xrightarrow{=(+47^\circ\mathrm{C})} \mathrm{B}_4 \xrightarrow{\approx(-70^\circ\mathrm{C})} \mathrm{Cr}$$

Symbols ($\approx$) and ($=$) refer to transition temperatures determined using X-ray and DSC measurements, respectively.

Dielectric dispersion as well as absorption were calculated from the data obtained with HP set-up in a wide frequency range of 0.01–1.5 MHz. LINKAM 5 μm cells was used as capacitor and this was calibrated. We were unable to orient the sample by a magnetic field. So, the sample was oriented by the surface effect. The cells consisted of two glass plates coated with a very thin conducting ITO (Indium Tin Oxide) layer. ITO layer produces a planar alignment. Finally, the long molecular axis is oriented in the plane of the substrate. Also the triangular voltage wave was applied to observe the ferroelectric-like-switching in an 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.

The X-ray studies were performed on X'Perrt PRO (PANalytical) diffractometer using the Cu Kα radiation ($\lambda = 1.54178$ Å) and a graphite monochromator. The sample was placed in a nickel-plated copper sample holder of dimensions $18 \times 9 \times 0.2\,\mathrm{mm}^3$. The temperature of the sample was stabilized (accuracy ±0.1°C) with the continuous flow cryostat supplied by Anton Paar Co. The sample was not oriented. Prior to the temperature measurements the sample was melted, next cooled to room temperature with the rate of 10 deg/min, and next left for 24 hours at this temperature. After this relaxing time the sample was cooled down to LN_2 temperature with rate 10 deg/min, and finally left for 12 hours. The patterns were obtained at rising temperature. After each heating stage the sample was allowed to equilibrate for about 10 min. To analyse and fit the spectra, the profile-fitting program FULLPROF [5] based on Rietveld method was used.

RESULTS AND DISCUSSION

The Figure 1 presents the dielectric absorption data observed on heating and cooling. The complex dielectric constants ε^* observed

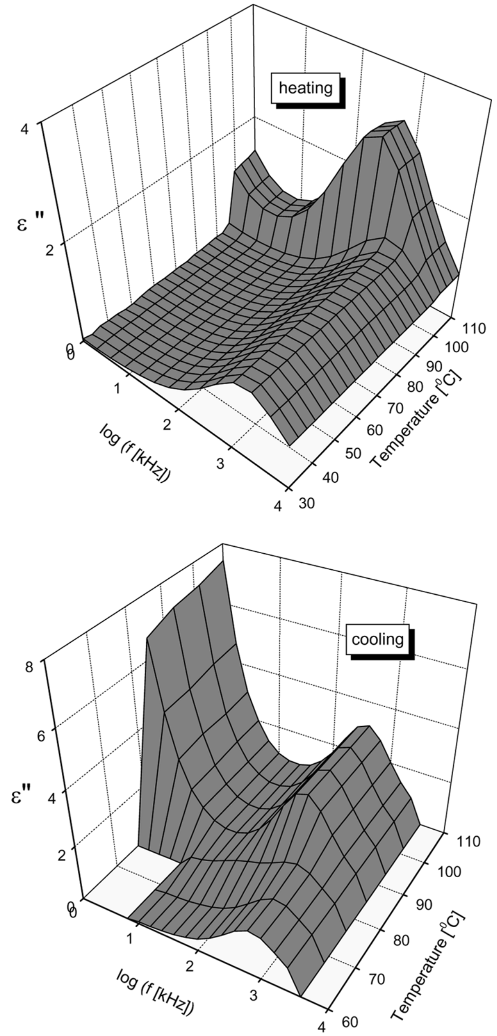


FIGURE 1 Dielectric absorption data observed on heating and cooling.

on heating were fitted to the real and the imaginary parts of Equation (1) to find the specific molecular dynamics of the B_4 and B_3 crystal-like phases.

Assuming a single molecular dipole relaxation as the effective response of an investigated system to an alternating field of frequency ω, $\varepsilon^*(\omega)$ should be presented in the form of the Debye equation

$$\varepsilon^*(\omega) = \varepsilon'_\infty + \frac{(\varepsilon'_s - \varepsilon'_\infty)}{1 + i\omega\tau_D} \tag{1}$$

where symbols "s" and "∞" stand for low and high frequency limits of an electric field. The single characteristic time constant τ_D, is called the *Debye relaxation* time. In Figure 2 Cole–Cole plot for B_4 phase (on heating at 40°C) together with fitting curves are presented. It is shown here that the observed process is characterized by the single relaxation time of $\tau_D = 0.3\,\mu s$. Going towards the clearing point it is discovered that the reorientation under discussion is temperature independent till the transition point (as is seen in Fig. 3). The total dipole moment of F-490 ($\mu = 5.413\,D$) is almost perpendicular to the long molecular – the long molecular axis is the axis of the lowest moment of inertia; it should be about parallel to the connection line in the middle ring between the meta positions where the long substituents are bound) [6]. Therefore, we suggest the observed Debye-like process in the B_4 and B_3 phases during heating is due to reorientation of the rigid core about the long molecular axis.

In the isotropic state where the three-dimensional long range order disappears, the process under consideration becomes the activation

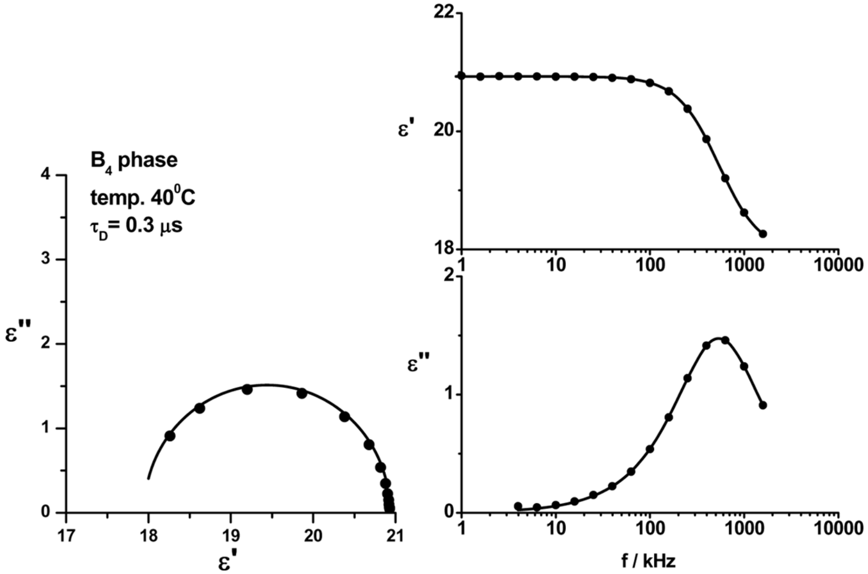


FIGURE 2 Cole–Cole plot for B_4 phase at 40°C (on heating) together with fitting curves.

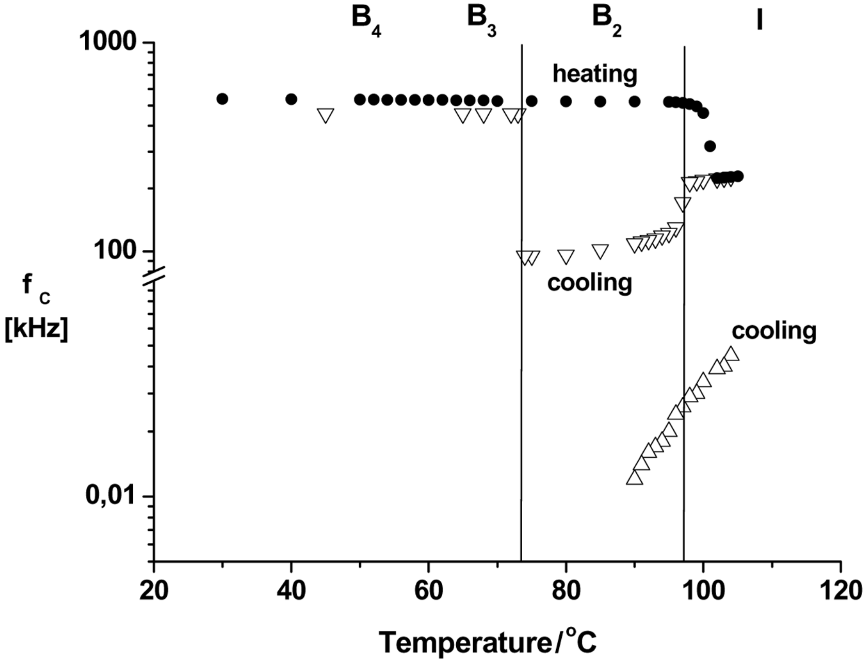


FIGURE 3 Critical frequency during heating and cooling versus temperature.

one both on heating and on cooling. For instance the Cole–Cole distribution parameter α is equal 0.03 and the relaxation time τ is 0.5 μs at 101°C. An activation energy of $(11.0 \pm 0.3)\,\mathrm{kJ\,mol^{-1}}$ is related to the reorientation of the molecules about the long axes.

On cooling, when B_2 phase have been achieved, foregoing process becomes a Cole–Cole reorientation with α-parameter increasing with decreasing temperature. An increase of more than 10% (up to 0.4) allows us to decompose Cole–Cole arc into two Debye-like processes. Within B_2 phase the Cole–Cole process fall into the kHz frequency range. So, we assume that the faster kilohertz Debye-like process may be due to reorientation of the terminal groups of the F-490 molecule with an activation energy of $(23.0 \pm 0.7)\,\mathrm{kJ\,mol^{-1}}$. The slower kilohertz Debye-like process may be connected with the conformational motion with an activation energy of $(45.0 \pm 1.5)\,\mathrm{kJ\,mol^{-1}}$.

According to the Nordio-Rigatti-Segre theory, in the isotropic phase, one might observes two main processes. It should be noted that "the cooling results" for the isotropic and B_2 phases, allow us to say that the second main process (low frequency one) is present. To extract these specific data we excluded a conductivity contribution from the complex dielectric constants ε^*. We got a few points to fit Debye semicircle to the low frequency data. In succession the critical frequency were estimated. Keeping in mind relatively high uncertainty of these data, we obtained a straight line, plotting the critical frequency versus temperature – see Figure 3. There is no step of the data at the transition point I – B_2 indicating that there is no influence of the phase transition. This means that the low frequency process is independent on conductivity change at I – B_2 transition point. So, in turn, it indicates that resulting process is of molecular origin. Taking into account relatively high value of ε' we suggest a strong positive dipole correlation forming dimmers (molecular pairs) or ferroelectric order in the short range. Finally, for this reason, we interpret the low frequency process as a linear response of statistically oriented ferroelectric clusters.

The Figure 4. shows diffraction patterns as a function of temperature. To see more details, the indexed diffraction pattern of F-490 is presented in Figure 5. One can see the lines correspond to a monoclinic base-centered phase (the space group P 1 1 b) with lattice parameters $a = 15.98\,\text{Å}$, $b = 15.17\,\text{Å}$, $c = 46.11\,\text{Å}$ and $\gamma \approx 90\,\text{deg}$. The temperature changes of the γ angle are smaller than 0.1 deg in the whole range of temperature and its error bars are comparable to the value of it. That

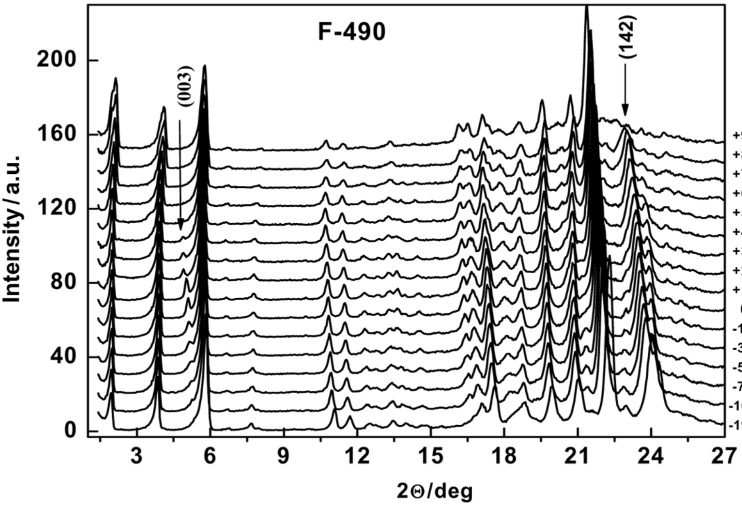


FIGURE 4 The X-ray diffraction patterns vs. temperature for the F-490 sample.

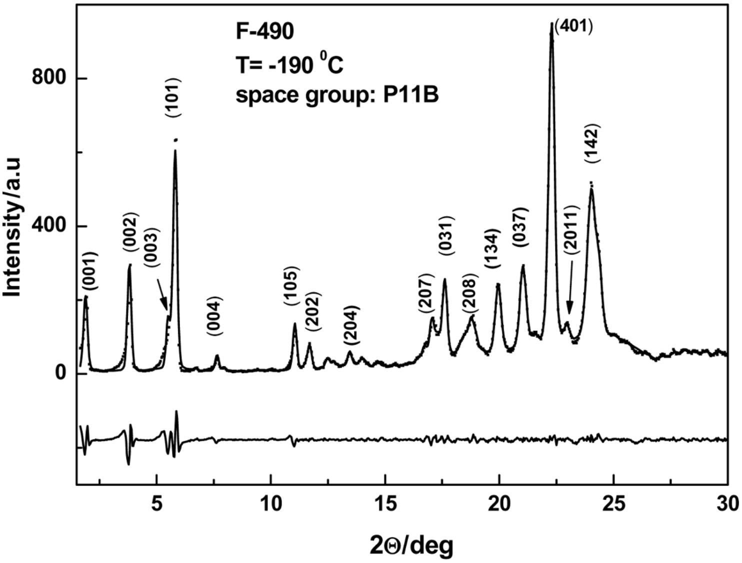


FIGURE 5 The X-ray diffraction pattern for the F-490 taken at −190°C. Points represent the experiment result, the solid line is the fitted pattern and below the differential one.

is why we do not present an extra figure for it. So small changes of γ could suggest the orthorhombic phase (i.e. P b a 2), however *U,V,W* – half-width parameters reached non-physical, huge values which could show the lower symmetry.

The orthorhombic structure P b a 2 transforms very easy to the monoclinic P 1 1 b structure. For the former structure $\chi^2 \sim 80$ and for the letter one $\chi^2 \sim 12$ what in the case of the liquid crystal we can think as a very good agreement. The Figure 6 presents lattice parameters and the volume cell of the F-490 vs. temperature.

Looking at Figure 4 one can notice the disappearing of the line (003) above +50°C and the line (142) above +80°C. These temperatures good correspond to characteristic ones obtained from DSC measurements, suggesting phase transitions. It is observed minimum of lattice parameter c at temperature $\sim +50$°C, as well. However, insignificant minima observed at $\sim +30$°C for lattice parameters a and b, and a little deeper for the volume cell of the F-490 do not correspond to the proposed phase diagram. It can suggest the changes of the lattice parameter c are mainly responsible for phase transitions.

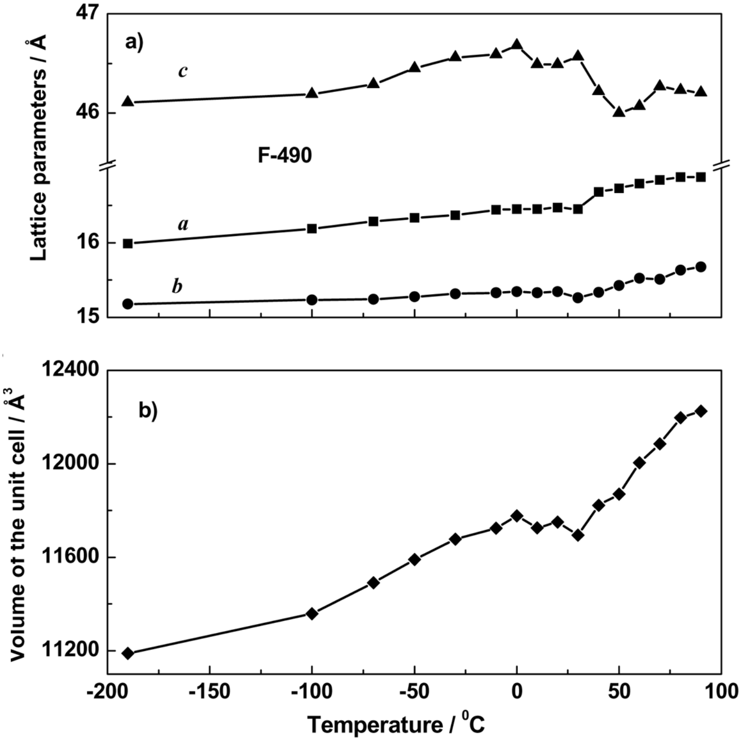


FIGURE 6 The temperature dependence of a) lattice parameters obtained for monoclinic phase sample and b) the volume cell of the F-490. Error bars are comparable with the symbol size.

CONCLUSION

The newly synthesized banana–shaped molecule named in short F-490 forms liquid crystalline structure B_2 in monotropic way (on cooling). This phase is antiferroelectric. The solidification process is influences by the cooling rate. The properties shown on cooling strongly depend upon thermal history of the sample. There is the Debye-like process seen in the B_4 and B_3 phases during heating. It is due to reorientation of the rigid core about the long molecular axis. On cooling, within B_2 phase, the Cole–Cole process fall into the kHz and has to be decompose into two Debye-like processes. The faster one may be due to the reorientation of the terminal groups of the F-490 molecule, the slower one may be connected with the conformational motion. The low frequency process seen on cooling has been interpreted as a linear response of statistically oriented ferroelectric clusters. At the lowest temperature the F-490 crystallizes in the monoclinic base-centred structure

P 1 1 b which on heating transforms to the orthorhombic structure P b a 2.

REFERENCES

[1] Pelzl, G., Diele, S., & Weissflog, W. (1999). *Adv. Mater.*, *11*, 707.

[2] Nori, T., Sekine, T., Watanabe, J., Furukawa, T., & Takezoe, H. (1996). *J. Mater. Chem.*, *6*, 1231.

[3] Heppke, G., Kruerke, D., Loehning, C., Loetsch, D., Rauch, S., & Sharma, N. K. (1997). *Freiburger Arbeitstagung Fluessige Kristalle*, Poster P70.

[4] Rouillon, J. C., Marcerou, J. P., Laguerre, M., Nguyen, H. T., & Achard, M. F. (2001). *J. Mater. Chem.*, *11*, 2946.

[5] Rodriguez-Carvajal, J. (1990). *Abstract Satelite Meeting on Powder Diffraction, Congr. Int. Union of Crystallography, Toulouse, France*, 127.

[6] D. Demus, private information.