Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

The Effect of Shearing on the Phase Retardation of Banana Liquid Crystals

S. Goldbach-Aschemann [a], Th. Rasing [a], R. Achten [b], A. T. M. Marcelis [b] & E. J. R. Sudhölter [b]

[a] IMM, Radboud University of Nijmegen, Nijmegen

[b] Laboratory of Organic Chemistry, Wageningen University, Dreijenplein Wageningen, The Netherlands

Version of record first published: 31 Aug 2006

To cite this article: S. Goldbach-Aschemann, Th. Rasing, R. Achten, A. T. M. Marcelis & E. J. R. Sudhölter (2005): The Effect of Shearing on the Phase Retardation of Banana Liquid Crystals, Molecular Crystals and Liquid Crystals, 437:1, 295/[1539]-301/[1545]

To link to this article: http://dx.doi.org/10.1080/15421400590954920

Mol. Cryst. Liq. Cryst., Vol. 437, pp. 295/[1539]–301/[1545], 2005

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590954920

The Effect of Shearing on the Phase Retardation of Banana Liquid Crystals

S. Goldbach-Aschemann
Th. Rasing
IMM, Radboud University of Nijmegen, Nijmegen

R. Achten
A. T. M. Marcelis
E. J. R. Sudhölter
Laboratory of Organic Chemistry, Wageningen University, Dreijenplein Wageningen, The Netherlands

The phase retardation of several banana type liquid crystals in their B_1 and B_2 phases is measured using a temperature controlled shear cell. In different phases the LC-cells are sheared to improve their order and the phase retardation before and after shearing is compared. It is shown that the phase retardation increases and the domain size enlarges as a result of shearing.

Keywords: alignment; birefringence; phase retardation; shear

INTRODUCTION

In the last decade [1] banana liquid crystals (BLC's) have attracted a lot of attention, in particular because of the presence of (anti)ferroelectric phases in these non-chiral systems [2]. However, experimental investigations are often hampered by the difficulty to obtain large enough single domain samples. In this paper we demonstrate how this problem can be solved by using a shear cell that includes a temperature controlled sample holder.

Part of this work was supported by the Stichting voor Fundamenteel Onderzoek der Materie (FOM) that is financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

Address correspondence to Th. Rasing, IMM, Radboud University of Nijmegen, Nijmegen. E-mail: th.rasing@science.ru.nl

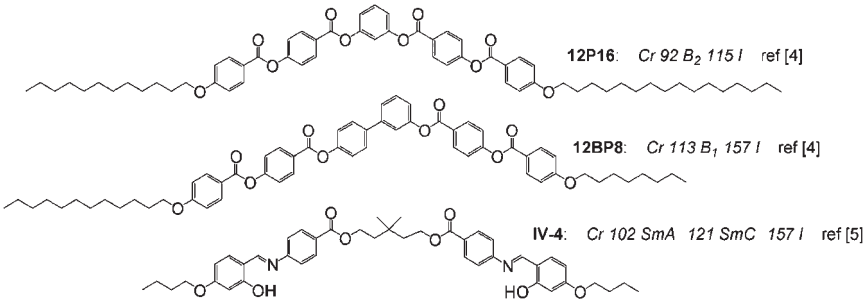

FIGURE 1 Structure of BLC's investigated.

Three banana-shaped compounds with different mesophase behaviour are used for these measurements. Compound 12P16 exhibits the smectic antiferroelectric B_2 phase. Compound 12BP8 shows the columnar B_1 phase (a two-dimensional periodic phase), whereas compound IV-4, with a dimethyl substituted central spacer, shows the unusual phase sequence SmA-SmC upon increasing temperature (Fig. 1) [4,5].

MEASUREMENTS

The beam of a stabilised He-Ne laser ($\lambda = 632{,}8\,\text{nm}$) was incident perpendicular to the samples and focused to a diameter of about 500 μm so that it traversed as few domains as possible (Fig. 2). A photoelastic modulater (PEM) and the shear cell were placed between two crossed polarisers. After the beam passed the second polariser it was focused into a diode whereafter the signal went to two lock-in amplifiers which also received the first respectively the second harmonic signal of the PEM. The 1f and 2f signals were sent to a PC which calculates with the use of the Jones matrix formalism the pase retardation of the beam by the sample. The combination of the PEM and the lock-in techniques yielded a sensitivity of a few hundreds of a degree.

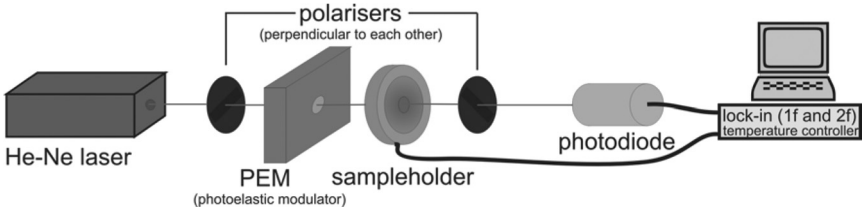

FIGURE 2 Set-up with the shear cell as the sampleholder.

This measurement technique implies that the phase retardation could only be measured for positive values modulo 90°. When going above or below 0° and 90°, the result was "folded" back unto the 0° to +90° region. The cooling curves, starting from the isotropic phase where the phase retardation should be minimal, showed that in most cases the phase retardation did not increase above 90°.

The phase retardation is directly proportional to the polarisation angle dependent refractive index difference $\Delta n(\alpha)$. This $\Delta n(\alpha)$ depends on the angle α between the laser beam polarisation and the optical axes of the domains that the beam crosses. Therefore, strictly speaking, $\Delta n(\alpha)$ here is not the birefringence Δn calculated with:

$$\Delta n = n_e - n_o = n_{\parallel} - n_{\perp} \tag{1}$$

But, using the ellipse equation

$$\frac{1}{n^2(\alpha)} = \frac{\sin^2(\alpha)}{n_o^2} + \frac{\cos^2(\alpha)}{n_e^2} \tag{2}$$

the angle dependent refractive index difference follows as:

$$\begin{aligned} \Delta n(\alpha) &= |n(\alpha) - n(\alpha - 90^\circ)| \\ &= \left| \frac{n_o n_e}{\sqrt{n_e^2 \sin^2(\alpha) + n_o^2 \cos^2(\alpha)}} - \frac{n_o n_e}{\sqrt{n_o^2 \sin^2(\alpha) + n_e^2 \cos^2(\alpha)}} \right| \end{aligned} \tag{3}$$

According to this formula and assuming a perfectly ordered sample, a rotation of the sample around the axis defined by the laser beam, should result in a measured phase retardation that changes four times from a maximum value to zero and back. If the phase retardation does not exceed 90° a polar plot should result in a clover leaf shape.

A Lakeshore 340 temperature controller was used to control the temperature between room temperature and 200°C with a precision of about 40 mK. For the angle dependent measurements, the shear cell was turned with a motion controller and the laser beam as the rotation axis.

With the shear cell it is possible to achieve a relative shear up to one millimeter amplitude between the two glass slides of a sample. At the same time, the distance between them only changes less than a micron, while the rotation axis stays at the same spot on the sample. A more detailed description of the shear cell can be found in reference [3].

All the samples are made of a pair of ITO covered glass slides with two stripes of 6 μm Mylar as a spacer. The empty cell is placed in the

shear cell which subsequently is heated to the respective temperatures of the isotropic phases. A measurement of the azimuthal angle dependence of the phase retardation was made to correct for any unintended optical anisotropies of the set up, especially of the glass slides of the samples. Then the cells were filled and the phase retardation measured during heating and cooling of the samples. The temperature change was slow (1K/min) to avoid temperature inhomogeneities. At certain points well within the different phases, the temperature was held constant to make an azimuthal scan or to shear the cells.

RESULTS AND DISCUSSION

In general, the phase retardation measurements as a function of temperature show clear jumps at phase transitions. As an example two cooling curves of LC 12P16 which contains the B_2 phase are shown in Figure 3. For both measurements, the residual phase retardation in the isotropic phase above 115°C was very low and due to internal stress of the glass plates of the samples. Cooling to the B_2 phase, the phase retardation started to increase to about 30° and, in the case of the non-sheared sample, remained at this value until crystallization occurred at 77°C. The sheared sample showed a big increase in phase retardation at the temperature at which the sample was sheared.

It must be noted here that the temperature dependent phase retardation was always measured at a certain fixed angle position.

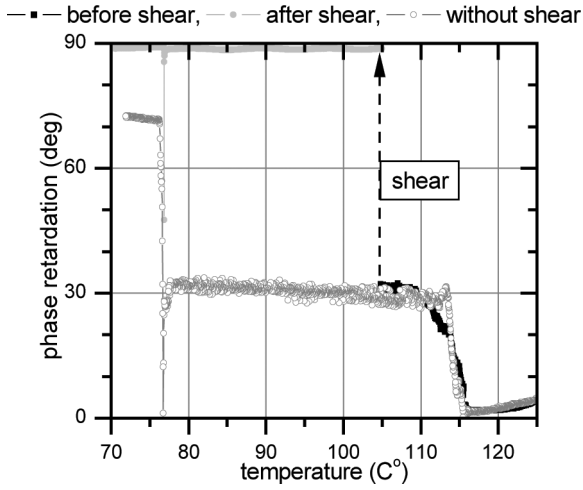

FIGURE 3 Temperature dependence of phase retardation of 12P16.

This specific position was mostly the angle of nearly maximum phase retardation after shear. Figure 4 gives the azimuthal angular dependence of the phase retardation, demonstrating even more dramatically the effect of shearing: whereas the non-sheared sample displays a very irregular polar plot, that of the sheared sample is a perfect clover leaf in accordance with Eq. (3). These results were typical for all samples, though in some cases they had to be sheared a second time to achieve a perfectly regular shape. From this it can be concluded that the non-sheared samples had no long range order alignment and that the laser beam always crossed several domains of different orientations.

Mostly, one of the maxima of the polar plot corresponded with the shear direction. In certain phases, for compound 12BP8 that shows a columnar B_1 phase, shearing never resulted in a four lobes pattern. During successful shearing it could often be observed by eye that the scattering of the samples decreased, confirming the creation of large domains.

As already stated above, a regular clover leaf shape for the azimuthal dependence indicates that the sample is aligned within the whole region that is traversed by the laser beam. Therefore, the results show that in most cases the order can be improved significantly by shearing the sample. The molecules try to minimize the torque by aligning their major axis perpendicular to the direction of movement of the glass plates. In phases like the B_1, which is columnar, this is

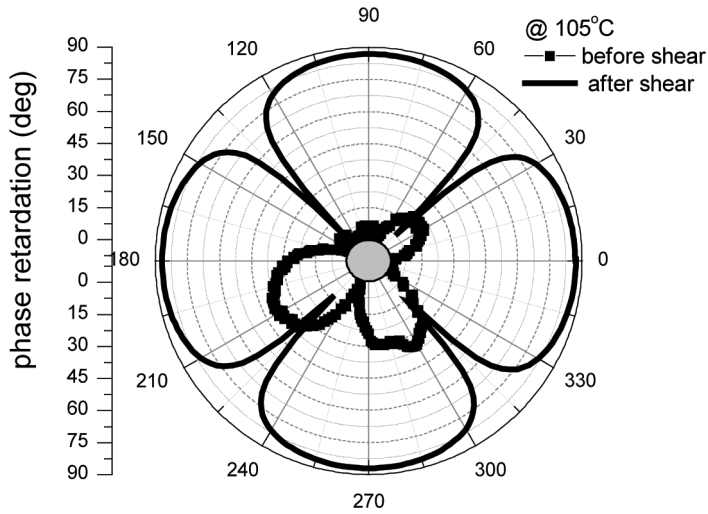

FIGURE 4 The effect of shear in the B2 phase of the banana LC 12P16.

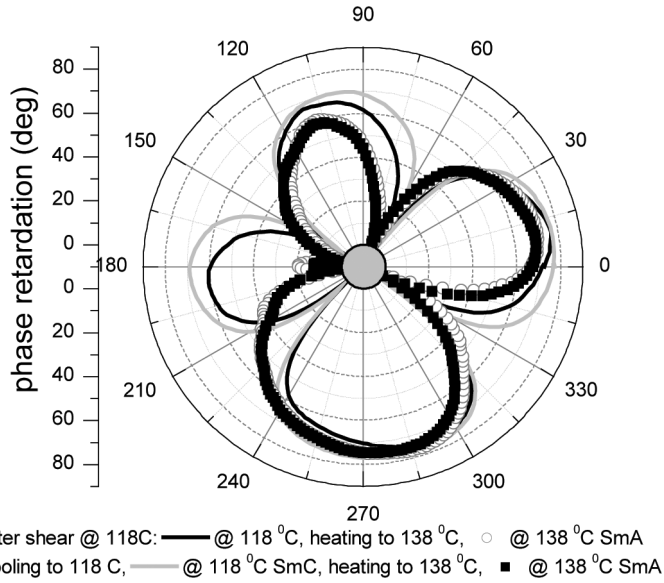

FIGURE 5 Phase retardation of IV-4 in the SmC and SmA phases after being sheared at 118°C.

not possible and therefore shear cannot improve the order. As a result, domains with different orientations of the optical axis within the beam remain and thus the measured curves have an irregular shape with many lobes.

In one sample of IV-4 an interesting phenomenon could be observed (Fig. 5). After applying shear in the intercalated SmA phase at 118°C, an azimuthal angle scan was made showing an almost perfect clover leaf shape. Then the sample was heated to the tilted smectic phase (SmC) where one of the lobes nearly vanished. When cooled back to the intercalated SmA phase the four regular lobes reappeared.

CONCLUSIONS

We have demonstrated how shear can significantly improve the order in banana LC samples leading to almost perfectly aligned samples. These can be used to determine phase transition temperatures or to do further investigations with other methods. The fact that in some cases the order of a LC cannot be improved by shearing indicates for example the presence of a columnar phase. The measurements indeed showed that shearing does not improve the domain size in the columnar B_1 phase.

Azimuthal angle dependent measurements of the phase retardation can be used to ascertain whether shear was successful. If the order is increased, the direction of maximum phase retardation in the polar plot gives the direction of the optical axis.

REFERENCES

[1] Niori, T., Sekine, T., Watanabe, J., Furukawa, T., & Takezoe, H. (1996). *J. Mater. Chem.*, *6*, 1231.
[2] Link, D. R., Natale, G., Shao, R., Maclennan, J. E., Clark, N. A., Körblova, E., & Walba, D. M. (1997). *Science*, *278*, 1924.
[3] Rastegar, A. Wulterkens, G. Verscharen, H. Rasing, Th. & Heppke, G. (2000). *Review of Scientific Instruments*, *71* (12).
[4] Achten, R., Cuypers, R., Giesbers, M., Koudijs, A., Marcelis, A. T. M., & Sudhölter, E. J. R. (2004). *Liq. Cryst.*, *31*, 1167.
[5] Achten, R., Koudijs, A., Karczmarzyk, Z., Marcelis, A. T. M., & Sudhölter, E. J. R. (2004). *Liq. Cryst.*, *31*, 215.