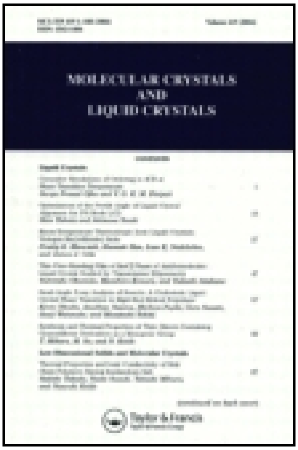

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Chirality in Discotic Lyomesophases

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Version of record first published: 24 Sep 2006

To cite this article: H. Sawade, I. Drevenšek Olenik, D. Krüerke & G. Heppke (2001): Chirality in Discotic Lyomesophases, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 367:1, 529-536

To link to this article: http://dx.doi.org/10.1080/10587250108028673

*Mol. Cryst. and Liq. Cryst.*, 2001, Vol. 367, pp. 529-536
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# Chirality in Discotic Lyomesophases

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Properties of isotropic and columnar cholesteric lyomesophases of triphenylene derivatives dissolved in dodecane were investigated by selective reflection (SR) and dynamic light scattering (DLS) spectroscopy. The selective reflection measurements reveal a strong dependence of the helical pitch on concentration and temperature, which can be explained by competing effects of the molecular twisting power and the intercolumnar steric forces. The DLS measurements reveal a presence of three relaxational type dynamic modes in the pre-transitional region of the isotropic-cholesteric phase transition. Two of these modes exhibit an arrhenius like temperature dependence and does not seem to be directly related with the transition. The third mode shows a critical slowing down near the transition temperature and is presumably related to the translational diffusion of the columnar stacks, which rapidly increase in their length with decreasing temperature.

*Keywords:* chiral liquid crystals; lyotropic; discotic; self-assembled systems; selective reflection

## INTRODUCTION

When discotic liquid crystalline materials are dissolved in apolar solvents, like hydrocarbons, a variety of highly viscous lymesogenic phases can appear[1,2]. The helical pitch of the cholesteric (Ch) and other chiral lyomesophases is very sensitive to the details of the molecular structure and usually depends strongly on temperature[3]. The appearence of the lyomesophases is presumably related to the orientational ordering of the finite-size columnar stacks of discotic molecules, which start to form already in the isotropic (I) phase and then grow in their length with increasing concentration[4] (Fig 1). This mechanism, which is quite common in aqueous solutions of the disc-shape molecules, is not evidently proved in case of apolar solvents. Consequently, the corresponding molecular self-assembling mechanism and structural modifications related to the formation of the stacks are not yet understood.

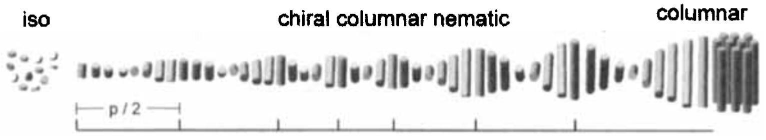


FIGURE 1 Model of the structural changes which could explain the variation of the pitch length with changing the concentration of the solvent in the chiral columnar phase.

We have recently reported on a phase diagram of the lyomesophases observed in the mixture of derivative DLT 2 (Fig 2) with dodecane[4]. At room temperature this mixture exhibits three different lyomesophases: two soft columnar phases and the columnar cholesteric phase. The later is observed for concentrations below *c* = 55 wt% DLT 2 in dodecane, while the Ch-I phase transition takes place at about c = 25 wt%, respectively. For concentrations below 25 wt% down to 10 wt% DLT 2 in dodecane, a remarkable induced birefringence can be detected when the material is exposed to the shear-flow. This observation suggests on the presence of strong pre-transitional phenomena in the DLT 2 - dodecane system. In this paper we report on the dynamical properties of the system in the pre-transitional concentration region which were studied by dynamic light scattering (DLS) experiments. We also report on investigation of the temperature dependence of the helical pitch of various solutions as determined from selective reflection (SR) spectroscopy.

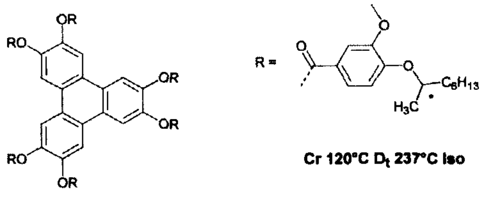


FIGURE 2 Structure and transition temperatures of the triphenylene derivative DLT 2.

## EXPERIMENTAL

The sample mixtures were prepared in the following way: A known quantity of the DLT 2 material was melted in a small pan. More dodecane than needed was added and the mixture was then heated up to 200°C for a few seconds. After cooling the mixture to room temperature it was weighed and the composition was calculated and, if necessary, heated up again to loose more dodecane to obtain the favoured composition. The mixture was introduced into a flat test cell and the two glass substrates were sealed together with a two-component epoxy resin.

To investigate the temperature and concentration dependence of the selective reflection we used planar aligned cells prepared by either using Teflon coated glass plates[5] or by the shearing technique. The sample was placed in a hot-stage (Linkam LTS 350) and illuminated with white light. The reflected light was analysed by a spectrophotometer (PR-703A Spot Spectrascan with PR-702A Spectrascan Console). The spectra were recorded on a computer that was equipped with a suitable spectra analysing program.

DLS experiments were performed in the mixtures of three different concentrations: $c = 33$ wt% of DLT 2 in dodecane, $c = 21$ wt%, and $c = 10.5$ wt%, respectively. The $c = 33$ wt% sample exhibited a cholesteric texture at room temperature and had a clearing point at about 100 °C. The other two samples were isotropic at all the investigated temperatures. The mixtures were introduced into planar cells made from two clean glass plates separated by 80 μm spacers and mounted into the hot-stage (Instec HS1-i). These cells had no surface alignment layers. The DLS measurements were performed using an ALV 5000 digital correlator and a He-Ne laser ($\lambda$ = 632.8 nm) as a light source. The incident angle of the laser beam with respect to the sample normal was 18°. Scattered light from the sample was detected at the scattering angle of $\theta = 60°$ and the normalized homodyne intensity autocorrelation function $g^{(2)}(t) = \langle I(0)I(t)\rangle / \langle I(t)\rangle^2$ was measured. The polarization of the incident laser beam was always perpendicular to the scattering plane ($s$-polarization), while the polarization of the scattered light was selected to be either perpendicular ($s$-polarization) or parallel ($p$-polarization) to the scattering plane. In the Gaussian approximation the normalized field correlation function of the scattered light $g^{(1)}(t) = \langle E(0)E(t)\rangle / \langle E(t)\rangle^2$ is related to $g^{(2)}(t)$ by the relation[5]

$$g^{(2)}(t) = 1 + \alpha \left| g^{(1)}(t) \right|^2, \tag{1}$$

where $\alpha$ is the spatial coherence factor depending on the apparatus. The dynamic response of the sample is expressed by the field correlation function of the form

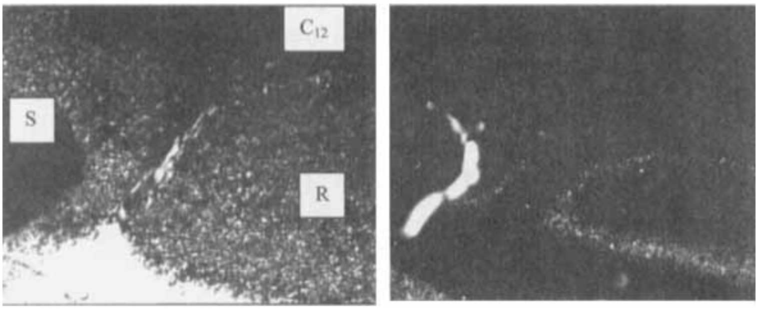
$$g^{(1)}(t) = \sum_i A_i e^{-t/\tau_i}\,, \tag{2}$$

where $A_i$ is the amplitude and $\tau_i$ is the relaxation time of the $i$-th dynamic mode. The corresponding diffusion coefficients of the modes may be calculated as $D_i = 1/\tau_i q^2$, where $q \approx (4\pi/\lambda)\sin(\theta/2)$ is the scattering wave vector.

## RESULTS AND DISCUSSION

### Selective reflection measurements

In order to get an impression how enantiomeric excess, temperature and solvent concentration influence the helical twist in the columnar nematic lyomesophase, we studied ternary contact preparations between the DLT 2 enantiomers and dodecane. As shown in figure 3 the contact preparation shows two large distinct regions, the left one is a region of the (*S*)-enantiomer, the right on is a region of the (*R*)-enantiomer. They both display a cholesteric texture with an unusual concentration behavior of the cholesteric pitch. The wavelength of the reflected light is decreased with increasing concentration of the chiral material. At a certain composition this dependence is reversed and the pitch increases with increasing triphenylene concentration. As expected, in the region of the racemic mixture in the middle of the contact zone between the (*R*)- and (*S*)-enantiomer, a non twisted nematic texture is observed. Furthermore, the variaiton of the enantiomeric excess shows an normal behavior of the selective reflection. The helical pitch is decreased by decreasing the enantiomeric excess, reflecting the helical twisting power of DLT 2.



a) b)

FIGURE 3 Photomicrograph of a contact preparation of DLT 2 (R) (left), DLT 2 (S) (right) and Dodecane at 41°C (a: reflection, b: transmission)

Fig 4 shows the temperature dependence of the helical pitch of the DLT 2 – dodecane mixtures for various concentrations. With our setup we can measure the pitch within the interval from 390 to 730 nm, the data are given only for limited temperature regions. Despite this limitation, however, one can evidently notice a rapid, almost linear increase of the pitch with increasing temperature. Such strong variation of the pitch can be explained by competing effects of the molecular twisting power and the intercolumnar forces (Fig 1).

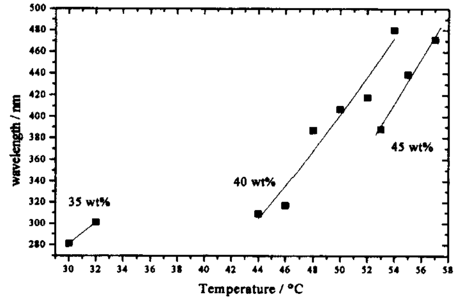
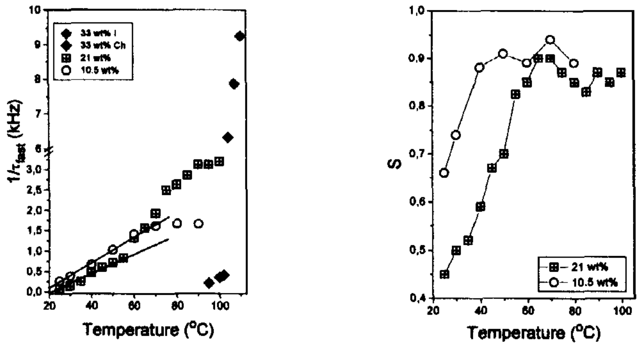


FIGURE 4 Temperature dependence of the pitch for various concentrations of DLT 2 in dodecane

## Dynamic light scattering measurements

The DLS autocorrelation functions detected in polarized (*s*-*s*) scattering regime exhibited two clearly separated dynamic modes, which we denote as the fast and the slow mode. The relaxation rate of the fast mode $1/\tau_{fast}$ is in the range of 0.1 kHz at room temperature and increases with increasing temperature (Fig 5 (a)). The increase, which is approximately linear at lower temperatures, is more pronounced in a more concentrated sample. In 33 wt% sample in addition a strong variation of the $1/\tau_{fast}$ is observed at the Ch-I phase transition, which suggest on different origin of the fast mode in different phases.



**a** **b**

FIGURE 5 Temperature dependencies of the relaxation rate (**a**) and the stretch exponent parameter (**b**) of the polarized (*s*-*s*) scattering fast mode.

Dependencies of $g^{(1)}(t)$ in the temporal region of the fast mode showed a considerable deviation from the exponential decay as given by Eq (2). A better fit could have been achieved by using a stretch exponential relation $g^{(1)}(t)=A_{fast}\exp((-t/\tau_{fast})^{\wedge}S)+\cdots$. The value of the parameter $S$ profoundly increases with increasing temperature, until it saturates at about $S = 0.9$ (Fig 5 (b)). The saturation in the more diluted sample (10.5 wt % of DLT 2 in dodecane) appears at lower temperature as in the 21 wt% sample, respectively. This feature together with the observed temperature dependence of the mode can be explained with the translational diffusion of the particles, which average length and polydispersity decrease with increasing temperature and decreasing concentration. These particles can possibly be the columnar stacks of the DLT 2 molecules.

The relaxation rate of the *s*-*s* scattering slow mode $1/\tau_{slow}$ is of the order of 0.1 Hz at room temperature and also strongly increases with increasing temperature (Fig. 6), exhibiting an Arrhenius type behaviour expressed as

$$1/\tau_{slow}(T) \propto e^{-W_a/kT}. \qquad (3)$$

The corresponding activation energy $W_a$ has a value of 1 eV for the 10.5 wt % sample and decreases to $W_a = 0.5$ eV for the 33 wt% sample. The variation of the $1/\tau_{slow}$ across the Ch-I transition in the 33 wt % sample is considerably lower than in case of the fast mode and suggests that the slow mode is of the same origin in both phases.

The intensity of the depolarized *s-p* scattered light in isotropic solutions was in general about 50 times lower than the intensity of the *s-s* scattered light. The corresponding DLS autocorrelation functions revealed a single exponential relaxation. The corresponding dynamic mode has a relaxation rate $1/\tau_{s\text{-}p}$ of about 0.1 kHz at room temperature (Fig 7). Similarly to the slow mode of the *s-s* scattering, this mode also shows the Arrhenius type dependence on temperature with activation energies of 1.05 eV ($c$ = 21 wt%) and 1.6 eV ($c$ = 33 wt%) respectively. In 10.5 wt% sample the *s-p* DLS signal was very low and consequently only the value of $1/\tau_{s\text{-}p}$ at room temperature is given. In 33 wt % sample a large modification of the $1/\tau_{s\text{-}p}$ is notable at Ch-I transition. However, as the s-p scattering is much stronger in the cholesteric phase than in the isotropic phase, we believe that the *s-p* mode in the cholesteric phase is actually equivalent to the *s-s* fast mode which becomes predominant due to the "mixing" of the modes in our orientationally unaligned samples.

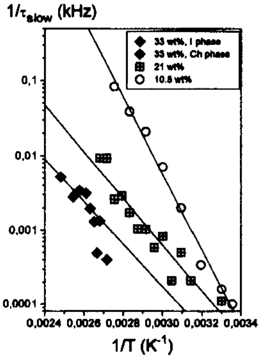


FIGURE 6 Dependence of the relaxation rate of the polarized (*s-s*) scattering slow mode on inverse temperature. Solid lines are fits to relation (3).

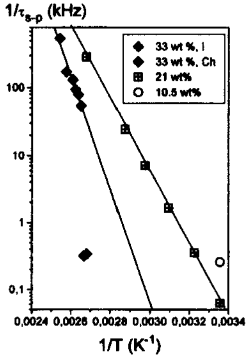


FIGURE 7 Dependence of the relaxation rate of the depolarized (*s-p*) scattering mode on inverse temperature. Solid lines are fits to relation (3).

## CONCLUSIONS

The selective reflection measurements in the cholesteric phase of the DLT 2 – dodecane system and polarization microscopy of the samples in contact preparation reveal a strong dependence of the helical pitch on temperature and concentration of various enantiomeric species. These features indicate the presence of several competing effects which determine the macroscopic chirality of the material.

The DLS measurements in the pre-trasitional region of the I-Ch phase transition reveal a presence of the critical relaxation mode which exhibits an about $1/\tau_{fast} \propto (T-T^*)$ dependence close to the transition temperature. This type of pre-transitional behaviour is usually related to critical fluctuations of the nematic order parameter[6]. In our case, however, it appears only in polarized scattering, so it is most probably associated with the translational motion of the columnar aggregates which strongly grow in size when approaching the transition temperature. In addition to this mode, the two modes with the Arrhenius type dependence on temperature were also observed. As the corresponding intensity of the scattered light varied only slightly with temperature, we relate their temperature behaviour with a temperature variation of the effective viscosity coefficients of the modes. Similar variation is, for example, known to determine the temperature dependence of the orientational normal modes in the lyotropic nematic phase[7]. The nature of the Arrhenius type modes in our system is for the moment not yet clear. It is possible that these modes originate from weakly birefringent orientational fluctuations of the local discotic orientational order, which in the pre-transitional region becomes superimposed with the additional columnar self-assembling. Further investigations of the corresponding dispersion relations of the modes, and additional dependencies on concentration, are in progress in order to achieve a better understanding of the observed features.

## Acknowledgments

This work is financed by the European TMR Network Project 'SILC'.

## *References*

[1] S. Chandrasekhar, B.K. Sadashiva, K.A. Suresh, N.V. Madhusudana, S. Kumar, R. Shashidar, G. Ventkatesh, *J. Phys., France,* **40**, C3 120 (1979).

[2] N. Usol'tseva, K. Praefcke, D. Singer, B. Gündogan, *Liq. Cryst.* **16**, 617 (1994).

[3] L.E. Blixth, I. Drevensek, G. Heppke, D. Krüerke, H. Sawade, presentation at annual Liquid Crystal Workshop, Freiburg, Germany, 2000, book of abstracts, P32.

[4] D. Krüerke, P. Rudquist, S.T. Lagerwall, H. Sawade, G. Heppke, *submitted to Ferroelectrics*, 1999.

[5] B.J. Berne, R. Pecora, *Dynamic light scattering*, Wiley, 1976, New York.

[6] J.D. Litster, T.W. Stinson, *J. Appl. Phys.* **41**, 996 (1970).

[7] M. Čopič. T. Ovsenik, M. Zgonik, *Liq. Cryst.* **2**, 643 (1987).