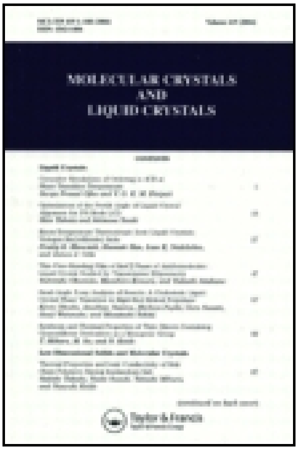

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Reorientation of Molecules in Magnetically Doped Discotic Liquid Crystal

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Reorientation of Molecules in Magnetically Doped Discotic Liquid Crystal

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The influence of the spheroidal Co-Fe magnetic particles on the orientation of discotic liquid crystal molecules in the presence of minor magnetic field (~0.3 Tesla) has been demonstrated using FTIR spectroscopy.

Keywords: FTIR spectroscopy; discotic liquid crystal; magnetic particles

INTRODUCTION

The possibility of incorporating minute magnetic particles into structured and viscous media, such as thermotropic and lyotropic liquid crystals, glasses and polymers has been demonstrated for the last ten years [1-9]. These new systems offer a large domain of investigation, both as a special bi-dimentional ferrofluid and as an example of the compatibility between solid particles and structured liquids. They also have enormous potential for application in magneto-optical and electro-optical devices. In particular, Jin et al. have shown that the doping of conductive ferromagnetic spheres in a viscous medium results in a composite material which is optically transparent and electrically conductive. This material with high through-thickness conductivity is potentially useful for a variety of device applications such as write pads, touch-screens, sensors, and alarm devices.

The combination of a liquid crystal and magnetic fluid gives even more interesting results. A distinctive characteristic of liquid crystals is the anisotropic nature of their physical properties, which may manifest themselves when subjected to external (electric or magnetic) fields. The study of the effects of the applied electric fields has contributed significantly to our understanding of the physics of liquid crystals and laid the foundation for many of their technological applications. To obtain analogous effects with magnetic fields, high-field intensities ($\geq 10^{-1}$ Tesla) are required in order to overcome the typically minute anisotropy of the diamagnetic susceptibility, $\Delta\chi$, of liquid crystals. To circumvent this limitation, Crochard and de Gennes [2] proposed "doping" the liquid crystal matrix with ferromagnetic grains. In principle, this should make possible the coupling of the liquid-crystalline molecular orientation to weak external magnetic field. In the first experimental paper Rault [3] reported on the basic magnetic properties of a suspension of rod-like γ-Fe_2O_3 particles in a nematic liquid crystal (MBBA). Later, on the basis of data given in [2], lyotropic [4,5] and thermotropic ferronematic [6,7] and ferrosmectic [8] liquid crystals were prepared and studied.

However to our knowledge, no attempt has been undertaken to design a *thermotropic ferrodiscotic liquid crystal.* This combination is interesting from a number of points of view. In particular, discotic liquid crystals based materials have enormous potential for use as semiconductors, photoconductors [9-12] etc. The main problem, which exists for the development of material for these applications, is the realisation of mono-domain alignment of disc-like molecules into columns. Some discotic liquid crystals can be easily aligned in a magnetic field. However for this purpose a very strong magnetic field is required (≥ 2 Tesla) [13-15] and then only planar alignment of discotic liquid crystals can be achieved. The combination of discotic liquid crystals and magnetic particles provides for the possibility of using much smaller magnetic fields and the possibility to drive a different type of alignment (planar or homeotropic) when the direction of the magnetic field across the cell is changed.

Here we present the results of preliminary investigations into the effect of magnetic particles on the orientation of a discotic liquid crystal (DLC) using Fourier Transform Infrared (FTIR) spectroscopy and polarised-light microscopy.

EXPERIMENT AND DISCUSSION OF THE RESULTS

A hexa-decanoyloxy-rufigallol (Aq6n10) discotic liquid crystal synthesized by H. Bock [16] according to the method of Carfagna et al. [17] has been used for these investigations. The structure formula and phase sequences of Aq6n10 are shown in Fig. 1. The cell for the infrared (IR) measurements was prepared in the following manner [18-20]. Two nylon 6/6 coated ZnSe windows (upper and lower one) were heated up to a temperature of ~ 415° K (15° K above of the phase transition temperature of DLC to the isotropic liquid) and 3-4 mg of DLC was placed on of one of the windows. When the liquid crystal was melted, a few drops of magnetic fluid were added and mixed carefully with the liquid crystal. During this procedure the isopar-M, which is petroleum based compound, was mainly evaporated at this temperature, as observed during the mixing process. The concentration of magnetic fluid in the DLC was ~ 10 volume % at the beginning of the mixing. The concentration of the magnetic particles in Isopar M was approximately 50% by volume. This mean that we obtained ~ 5% of magnetic particles in the liquid crystal by volume. Following this preparation the second window was placed on top of the first one and the windows rotated with respect to each other in order to spread the substance uniformly between them. It should be pointed out that the discotic liquid crystal retains its properties after this procedure; this has been verified by means of the polarising microscope. Two different magnetic fluids were used in these experiments: an isopar-M solution of Co-Fe and Ni-Zn spheroidal magnetic particles with an average particle size of 92 Å for Co-Fe and 67 Å for Ni-Zn. These particles are characterised by different magnetic properties (in particular the internal magnetic field is the largest for the Co-Fe particles and smallest for Ni-Zn particles) [21].

In general magnetic fluids are colloidal suspension of ultra-fine single-domain particles of ferromagnetic or ferrimagnetic materials dispersed in a carrier liquid and stabilised by a suitable organic surfactant [21]. The particles have radii ranging from approximately 2-10 nm and as they are single-domain , they are considered to be in a state of uniform magnetisation with magnetic moment, m, given by:

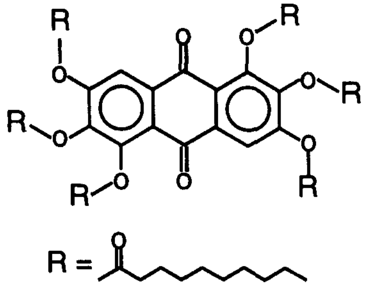
$$m=M_s v, \qquad (1)$$

where $M_S(T)$ denotes saturation magnetisation and v is the magnetic volume of the particle. The particles also have an anisotropic or internal field, H_A (A/m), where in the case of uniaxal anisotropy,

$$H_A=2K/M_S, \qquad (2)$$

$K(J/m^3)$ being the anisotropy constant.

The IR spectra in the wavenumber range 450-4000 cm^{-1} were recorded using a FTIR spectrometer. The IR cell was thermostated in a hot stage that was specially designed to fit the spectrometer, and to control temperature within ± 0.1° K [18-20]. We used this particular technique for the investigations of reorientation of the DLC molecules, since it is well know that the IR technique is a powerful tool for the study of structure and orientation of liquid crystals. This technique is particularly useful when information about the alignment and reorientation of molecules in the bulk of the DLC cell under certain external condition is required. Sometimes it is not easy to notice the change in the alignment of a DLC using a polarised microscope.



$R=OCOC_9H_{19}$; Cr-382 K-$D_{rect.}$-401 K-I

FIGURE 1 Structure and phase sequences for Aq6n10 discotic liquid crystal.

Before making the FTIR measurements, the liquid crystal cell was heated up to the temperature of isotropic phase of the DLC (~ 410° K). IR measurements were then performed at different temperatures during cooling from the isotropic phase to the discotic phase (~ 386° K). This is a routine procedure for obtaining uniform alignment for discotic liquid crystals. In order to investigate the influence of the magnetic particles on the alignment of the DLC, IR spectra at different temperatures were measured for the same cell: (i) without magnetic field and (ii) in the presence of magnetic field of ~ 0.3 Tesla. Fig. 2 shows the IR spectra of Aq6n10 in the region of 700-1900 cm^{-1} at temperature 386° K (in discotic phase) obtained as a result of procedure (i) (solid line) and procedure (ii) (dotted line). As can be can seen from Fig. 2, the result of the influence of the magnetic field (via magnetic particles) on the orientation of discotic liquid crystal molecules is quite obvious. This figure shows how the intensity of some vibrational bands decreases whereas the intensity of other increases. In particular, the intensity of C-H aromatic out of plane deformation observed in the wavenumber range 700-900 cm^{-1} almost doubles after application of the magnetic field.

Quite a big difference is also observed for C=O stretching vibration at 1770 cm^{-1} and at 1740 cm^{-1} (in alkyl chain) and around 1331 cm^{-1} (CH_3 symmetric bending) and 1100 cm^{-1} for C-H in plane deformations.

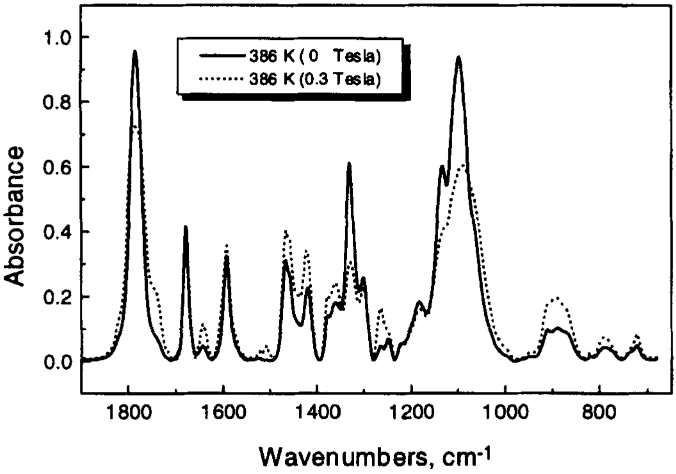


FIGURE 2 FTIR spectra of mixture of Aq6n10 discotic liquid crystal with Co-Fe magnetic particles (at concentration ~ 10 vol.%) in the mesophase (at temperature 386° K) after slow cooling from isotropic phase without magnetic field (solid line) and in the presence of magnetic field ~ 0.3 Tesla (dotted line).

As was shown in previous IR studies of the alignment of DLCs by means of FTIR spectroscopy [18-20], the alignment of DLCs in the presence of the orienting layer (Nylon 6/6 in particular) are mainly side-on (the core is oriented in the window plane). We can expect the same situation for Aq6n10. In fact, Fig. 3 demonstrates that at the beginning of discotic phase the temperature behaviour of the core's vibrational bands is mainly side-on. However it is also known that the cores of this particular discotic liquid crystal stack into the tilted columns in a discotic phase. This is probably why the intensity of some aromatic stretching vibration, oriented in the plane of the core, does not change much after the reorientation of the molecules in the presence of magnetic particles.

Nevertheless, the variation in intensity of the majority of vibrational bands leads to the conclusion that the orientation of discotic molecules has changed with respect to the window plane under the influence of magnetic field.

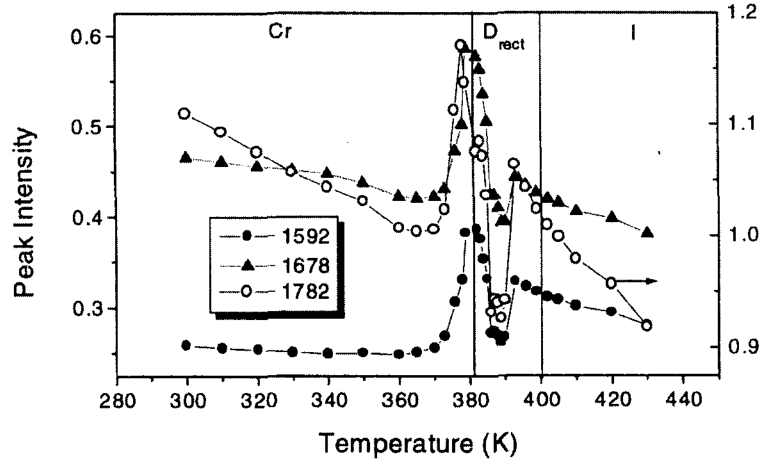


FIGURE 3. The dependence of the peak intensity of three vibrational bands on temperature for pure Aq6n10 contained in between nylon 6/6 coated ZnSe windows.

The IR study of the mixture of Aq6n10 with Ni-Zn spheroidal particles shows that the effect of these particular magnetic particles on the orientation of discotic liquid crystal is much smaller. Furthermore for the case of the isotropic phase of the DLC with both types of particles no changes were observed in IR spectra measured before and after the application of the magnetic field (application time ~ 1.5 hours).

The observation of the liquid crystal cell under the polarised-light microscope was performed before and after the aforementioned IR measurements. These investigations show that magnetic particles were uniformly distributed in the bulk of the DLC cell before the application of the magnetic field. However, as can be seen from Fig. 4, after the magnetic field has been applied for five hours, the magnetic particles form chain structures. This is due to the fact that magnetic field (~0.3 Tesla) is still quite large and causes the stacking of magnetic particles. This in turn causes a non-uniform effect of magnetic particles on the orientation of the DLC in the bulk. In order to avoid this effect, a smaller magnetic field can be used from one side. Furthermore, needle shaped magnetic particles can possibly also increase the effect of the orientation of DLC molecules, since it is probably easier for magnetic particles with such a shape to penetrate to the intercolumnar space.

The influence of magnetic particles on the orientation of discotic liquid crystals in the presence of a minor magnetic field has been demonstrated using FTIR spectroscopy. However in order to use this effect as a method for the achievement of the certain alignment in a discotic liquid crystal cell, further investigations with magnetic particles of different shapes and sizes and with different types of discotic liquid crystals are necessary.

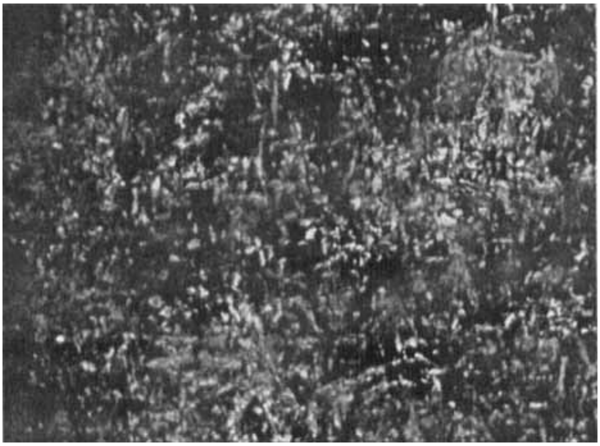


FIGURE 4 The structure of the mixture of Aq6n10 and Co-Fe magnetic particles observed at room temperature via polarized-light microscope.

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