

Orientational Order Parameter Measurements of Discotic Liquid Crystal

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Abstract. The IR dichroism technique is a convenient method which can be used to measure the molecular order parameter corresponding to the IR bands exclusively present in the disc-like molecules in discotic liquid crystal (DLC). To measure orientational order parameter, homeotropic alignment of discotic liquid crystal was attained by slow cooling of sample from isotropic phase on untreated flat CaF₂ substrate. The homeotropic alignment thus achieved was found to be thermodynamically stable in the discotic mesophase. IR spectra were recorded at different temperatures for the DLC. The order parameter was calculated by comparing the spectra of discotic phase with that of the isotropic phase. Order parameter has been presented as function of temperature for different significant IR bands present in the DLC.

Keywords: Discotic liquid crystal, infrared spectroscopy, orientational order parameter.

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INTRODUCTION

Since their discovery by Chandrasekhar in 1977 [1], discotic liquid crystals (DLCs) have attracted the attention of many research groups. Serious efforts have been made to exploit DLCs in organic electronic devices. A typical discotic mesogen generally includes a central aromatic core functionalized with three to eight flexible chains. Flexible alkyl chains around the cores substantially insulate the column from the neighboring column. Conductivity is, therefore, anticipated to be significantly higher along the column axis; therefore, the DLC columns are sometimes referred to as quasi-one-dimensional conducting wires. The phases formed by disc-like molecules are characterized by the degree of positional order and, in the case of the columnar phases, the symmetry of the two-dimensional lattice.

The two main types of mesophases DLCs form are nematic and columnar. Majority of DLCs show columnar mesophase which may be formed due to strong π - π molecular orbital overlap within the columnar stacks [2].

For applications such as advanced electronic materials knowledge about structural order in DLCs in terms of the orientational order parameter is essential.

In this paper we have presented orientational order parameter for some significant bands of a discotic liquid crystal as function of temperature. Fourier transform infrared spectroscopy has been used to measure the order parameter, the quality and the type of the alignment.

EXPERIMENTAL

The compound under present study is 5th homologue of 1-nitro-2,3,6,7,10,11-hexaalkoxytriphenylene [3] which shows a wide range of hexagonal columnar mesophase (Col_h) (Col_h 140°C Iso).

IR dichroism measurements were carried out using the IR spectrophotometer FTIR-8400 from Shimadzu. The sample was taken between untreated flat CaF₂ substrates. A 16 μ m mylar spacer was used to maintain a uniform thickness of the sample. Slow cooling of the sample from the isotropic phase yielded good homeotropic alignment as shown in figure 1(b). The spectra were obtained first in the isotropic phase and at various temperatures in the columnar phase. The dichroic ratio was calculated using the integrated absorption intensities corresponding to the different stretching modes and the corresponding order

parameters obtained as a function of temperature for pure DLC.

RESULTS AND DISCUSSION

For DLC, there are two possibilities for the alignment of molecules: (i) edge on or planar alignment in which the column axis is in the plane of the electrode, and (ii) face on or homeotropic alignment in which the disc column axis is perpendicular to electrode surface. In the present case when the sample was taken in a $16\mu\text{m}$ CaF_2 cell homeotropic alignment was obtained on slow cooling from isotropic phase and the alignment thus obtained is stable throughout the mesophase range as confirmed by the dark field view under crossed polarizers at different temperature (Figure 1(b)).

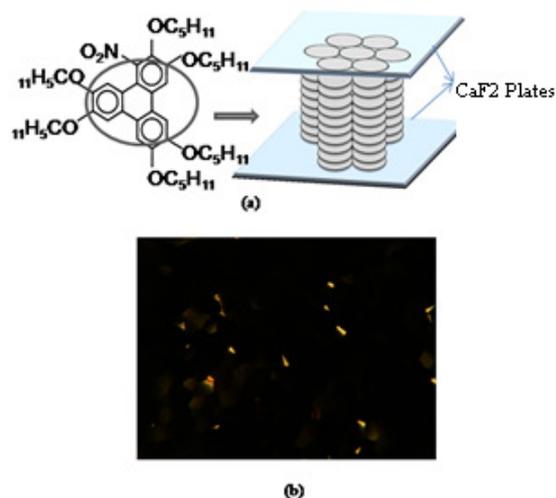


FIGURE 1. (a).Schematic representation of chemical structure of the DLC under study and and its homeotropic arrangement between CaF_2 plates. (b) POM image at 30°C .

Thus the molecules are arranged on the surface acts as nucleation site at which one disc stacks on the top of the other and self assemble in form of columns. We also studied the molecular arrangement in DLC cell by polarised infrared spectroscopy corresponding to C-C aromatic stretching band near 1617 cm^{-1} present in the DLC. Schematic representation of the interaction of the IR beam with a discotic material for homeotropic alignment is shown in figure 2. The peak intensity A was determined corresponding to these two bands at the difference between the absorbance at a band maxima and at a base line level. The absorbance profile for both bands in columnar hexagonal phase at room temperature is shown in figure 3. We observed that in both cases there is no significant angular

dependence of absorbance and discs are arranged in face on manner. These results are in agreement with those obtained from POM.

The infrared (IR) dichroism technique can be used to measure the orientational order parameter (S) in a liquid crystal. In the case of a discotic LC [4,5] $S = \frac{1}{2}(\cos^2\Phi - 1)$, where Φ is the angle made by the local director and the column axis (figure 2) and δ is the angle between the transition dipole moment p_i and the normal to the core [4]. When unpolarized IR radiation is used, the dichroic ratio is given by $R = \frac{I_{DLC}}{I_{IS}}$ where I_{DLC} and I_{IS} are the integrated absorption intensities in the liquid crystalline and isotropic phases respectively. In the case of the C-C in plane stretching vibration, ($\delta = 90^\circ$), $S = 2(R-1)$. And for the out of plane vibrations corresponding to C-H, ($\delta = 0^\circ$), $S = 1-R$.

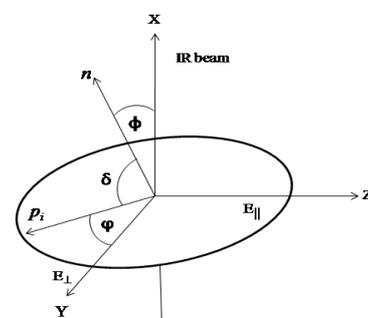


FIGURE 2. Schematic representation of the interaction of the IR beam with a discotic material for homeotropic alignment. [5].

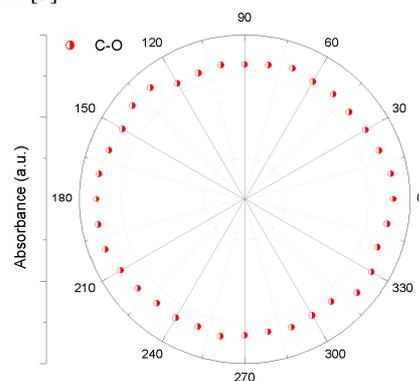


FIGURE 3. Polar plot of absorbance profiles for C-C aromatic stretching near 1617 cm^{-1} .

In DLC, the IR band near 1617 cm^{-1} corresponding to C-C aromatic stretching vibration has been found to be a sensitive indicator of ordering [6]. The calculated value of S corresponding to this vibrational band is $\cong 0.845$ (figure 4). This large value of S indicates the discotic cores are almost perfectly aligned by self organizations of discotic molecules. In general triphenylene based DLC have almost planar core and

due to intense π - π interactions between the cores causing TP cores to be almost normal to the column's axis.

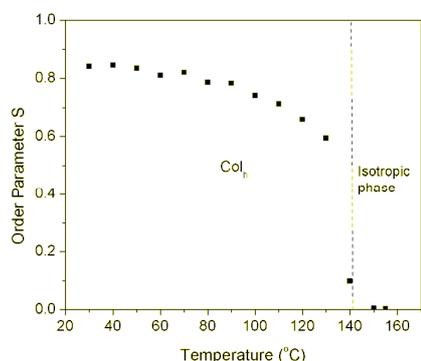


FIGURE 4. Order parameter S for the C-C aromatic stretching vibration near 1617 cm^{-1} .

A plot of S for C-O-C asymmetric stretching vibration near 1175 cm^{-1} is shown in figure 5. The maximum value of S is found to be 0.42.

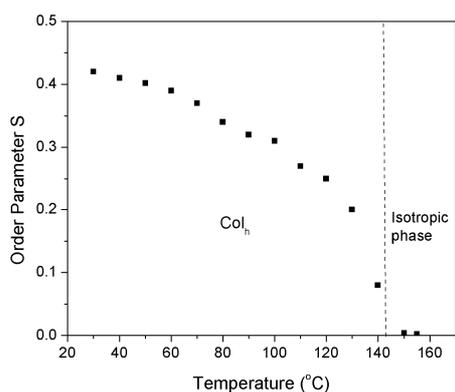


FIGURE 5. Order parameter S for the C-O-C stretching asymmetric vibration near 1175 cm^{-1} .

If we look at structure of DLC molecule Figure 1(a), we observed that C-O-C bonds are directly attached to the central core. But the direction of dipole moments associated with these vibrations are not exactly parallel to the plane of the core. Also they change with the change of the conformation of the molecule [6]. Therefore the observed value of S for C-O-C band is much lesser than that for the C-C aromatic stretching vibration near 1617 cm^{-1} . We also calculated S for C-O-C symmetric stretching near 1100 cm^{-1} . The plot of S as function of temperature for this band is shown in figure 6. We observed that this value is greater than that calculated for C-O-C asymmetric stretching vibrational band. This shows that the associated dipole moment for C-O-C symmetric vibrations are aligned more towards the direction parallel to the plane of the core as compared to the C-O-C asymmetric vibrations [6].

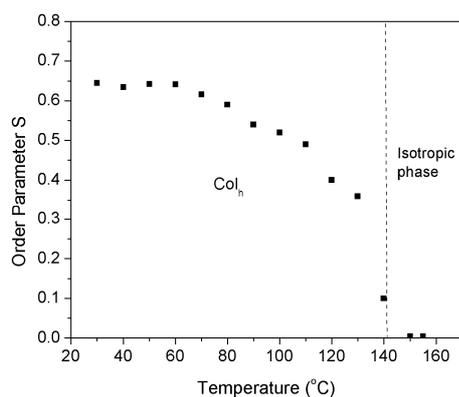


FIGURE 6. Order parameter S for the C-O-C stretching symmetric vibration near 1100 cm^{-1} .

CONCLUSIONS

The orientational order parameter measurements for mononitro triphenylene DLC has been carried out as a function of temperature for different significant IR bands using IR dichoric technique. Homeotropic alignment of pure DLC sandwiched between untreated CaF_2 substrate was obtained by slow cooling from isotropic phase. Our results show that IR dichoric technique is very useful in determining not only the order parameter of DLC but also the molecular arrangement in DLC. The TP based DLC has a high ordered central core which aligns almost in a direction normal to its column axis, giving a high S value around 0.845 for C-C inplane aromatic stretching vibrations near 1617 cm^{-1} . We also calculated S values for symmetric and asymmetric stretching vibrations near 1100 and 1174 cm^{-1} respectively. We observed that these values are much less than those calculated for C-C aromatic stretching vibrations because the directions of the dipole moments for these vibrations are not parallel to the core.

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