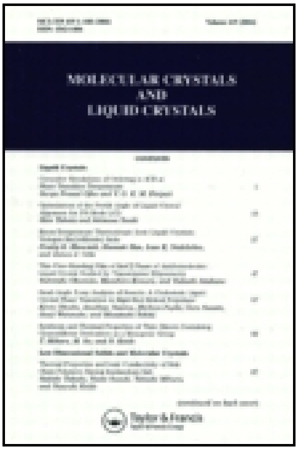

Molecular Crystals and Liquid Crystals

Order Parameter, Alignment and Anchoring Transition in Discotic Liquid Crystals

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To cite this article: Jagdish K. Vij, Antoni Kocot & T. S. Perova (2003): Order Parameter, Alignment and Anchoring Transition in Discotic Liquid Crystals, Molecular Crystals and Liquid Crystals, 397:1, 231-244

To link to this article: http://dx.doi.org/10.1080/714965593

Mol. Cryst. Liq. Cryst., Vol. 397, pp. 231/[531]–244/[544], 2003
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390214167

ORDER PARAMETER, ALIGNMENT AND ANCHORING TRANSITION IN DISCOTIC LIQUID CRYSTALS

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The results of our investigations show that on an untreated flat substrate, the discotic liquid crystals align side-on (or homeotropically) if the sample is slowly cooled from the isotropic phase. If the sample is kept in the glassy or crystalline state for several hours, the alignment inevitably changes to edge-on (planar or heterogeneously planar) in this phase. However, if the sample is heated from the glassy/crystalline phase, the alignment alters slowly from edge-on to side-on. This anchoring transition is dependent on the temperature and the substrate. On the other hand if the flat surfaces are treated with a polymer, the alignment achieved on cooling is also mostly side-on. A grooved surface or slightly uneven surface promotes the edge-on alignment (homogeneous and even heterogeneous). This type of alignment persists even when the surface is treated with a polymer. The side-on alignment once achieved is found to be thermodynamically stable in the discotic phase, where as the edge-on alignment has the lower energy in the glassy/crystalline phase. A plausible explanation is given.

Keywords: discotic liquid crystals; polarized IR spectroscopy; orientational order parameter

JKV thanks his former research students G. Kruk and S. Tsvetkov and former associates E. Hild, and R. Wrzalik for the work and the discussions on the discotics. H. Ringsdorf, O. Karthaus and S. Kumar are thanked for synthesizing and for supplying of the discotic liquid crystalline compounds. K. Merkel is thanked for her help in arranging the figures.

INTRODUCTION

S. Chandrasekhar [1] predicted the occurrence of mesophases in systems of disc-shaped particles and pointed out the fundamental importance of the mesophases so formed. Following that prediction, Chandrasekhar et al [2] synthesised compounds of benzene-hexa-n-alkanoates and carried out optical, thermodynamical and X-ray studies. Based on their X-ray structural investigations, they proposed the structure of the mesophase that they discovered. It is remarkable that the structure so determined for the first time has proven to be correct in the subsequent works carried out on the columnar phase in most discotics to-date. The columnar phase is a long-range ordered two-dimensional lattice, but with short range ordered and fluid-like arrangement in the 3rd dimension - in simple cases. A tremendous growth of interest during the last decade has been motivated by the scientific interest in the self-organising systems and the potential, as recently demonstrated, for technological applications of discotics. Some of these applications and the synthesis of new types of discotics are being discussed in the other articles of this special issue.

We have been interested in finding reasons as to why and how such large molecules organise themselves and the type of the order achieved on a flat substrate. Fourier transform infrared spectroscopy is used to measure the order parameter, the quality and the type of the alignment. Two types of orientational orders are possible, the side-on (or homeotropic) and the edge-on (or planar homogeneous and planar heterogeneous) (Figs. 1 and 2). We find that FTIR polarizing spectroscopy used in conjunction with polar-

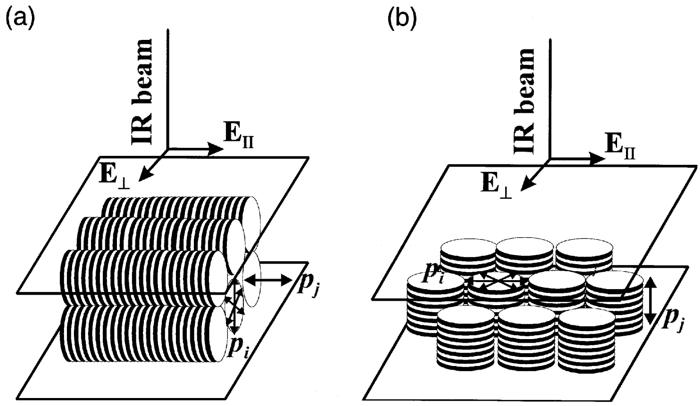

FIGURE 1 The orientation of the transition dipole moments for the in-plane and out-of-plane vibrations for the edge-on (*a*) and side-on (*b*) alignment of HPT in its columnar phase.

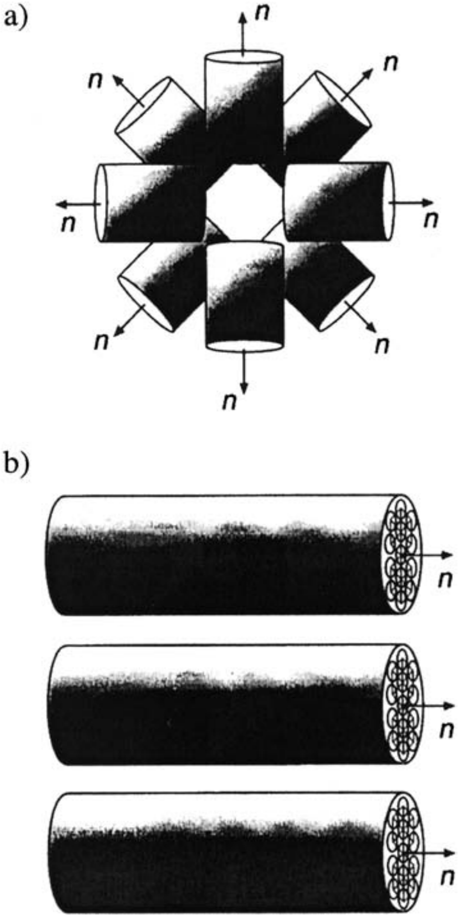

FIGURE 2 (a) Planar heterogeneous, local directors parallel to the substrate but randomly oriented, (b) Planar homogeneous, local directors parallel to the substrate and oriented in one direction.

izing optical microscopy is a powerful technique for finding the extent and the type of alignment and for determining the order parameter. The substrates on which the alignment of discotics has been achieved, and the surface treatments have been altered. Qualitatively, the disc-like shape of the molecules, the long-range van der Waals forces and the overlapping of the π electrons of the neighbouring benzene rings appear to be responsible for the self-organisation and the order in discotics. The motion of the alkane chains account for the fluidity/fluctuation of individual discs in the third dimension and this is mainly responsible for the mesophasic behaviour.

Nevertheless to our knowledge, no proper theory as to what triggers the self-order has yet been given. In this article, we review the contributions that we made in developing FTIR spectroscopic techniques for determining the order parameter, the type of alignment achieved on a number of substrates and in investigating the anchoring transition in discotics. The discotics investigated, are based on the triphenylene core.

ORIENTATIONAL ORDER PARAMETER AND METHODS FOR ITS DETERMINATION

The orientational order parameter, S, is defined as [3]

$$S = \frac{1}{2}\langle 3\cos^2\Theta - 1\rangle \tag{1}$$

Θ is the angle between the local director and the columnar axis (Fig. 3). The angle is distributed from column to column. In the column, the individual discs may also be tilted relative to each other, hence the angle Θ for the discs in the column may also be distributed. The ensemble average is taken over the entire sample. If the rotation around the axis normal to the disc is not free, then this will be reflected in the biaxiality of the molecule. Then a second parameter called Dispersion, D, need to be introduced [4]. For the analysis on discotics, we assume that the discs are uniaxial.

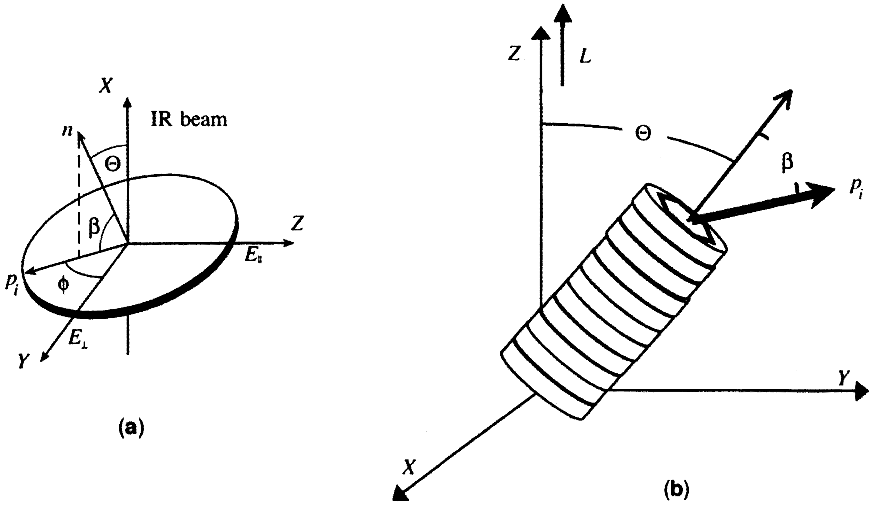

FIGURE 3 The interaction of the IR beam with a discotic material for (*a*) homeotropic and (*b*) planar orientation of molecules. Θ tilt angle, β polar angle.

The infrared spectroscopic technique has been developed for smectics for measuring both the order parameter S, and the dispersion parameter, D, arising from the biaxiality of the molecule where the phase formed is assumed to be uniaxial [4]. For smectic C*, where the phase on helical unwinding is biaxial [5], polar plots of absorbance vs. the angle of polarization can give information for both the polar and quadrupolar orders.

We have developed a number of methods for determining the order parameter in discotics [6] too. In this paper, we discuss two of the methods that can commonly be used. In the first, we use unpolarized IR beam and the second method can use both polarised and unpolarised beams.

First Method

For unpolarised beam, the dichroic ratio R_i is defined as [7]

$$R_i = \frac{I_D}{I_i} \tag{2}$$

I_D is the intensity of the IR band for the discotic phase and I_i is the intensity of the band in the isotropic phase. We define β as the angle between the normal to the core and the transition dipole moment vector, p_i (Fig. 3). For $\beta = 90^\circ$ i.e., for the C-C in-plane and C-O-C stretching vibrations

$$S = 2(R_i - 1) \tag{3}$$

For $\beta = 0^\circ$, such as for C-H out-of plane vibrations

$$S = 1 - R_i \tag{4}$$

The **second method** is based on measuring the spatial components of the absorbance for the discotics [8].

In the uniaxial columnar phase, the components of the absorbance, A_X, A_Y, A_Z can be expressed using the expressions obtained for a classical SmA phase, provided the dispersion parameter, D, is ignored.

For this analysis too, the disc is assumed to be uniaxial. The orthogonal co-ordinate system in the laboratory frame is related to the cell (Fig. 4). Axes Y and Z are fixed to the plane of the cell. When the IR is incident normally to the cell (Fig. 4a), X axis coincides with its propagation direction. When the cell is rotated around the Y axis, X and Z are also tilted (Fig. 4b). The absorbances, A_Y, A_Z, are measured for the normal incidence of IR beam. In order to measure A_X, the cell has to be tilted by an angle of 90°. This is however impracticable but can be determined from the measurements of absorbance $A(\alpha)$ as a function of α.

For a cell tilted at an angle of α, as shown in Figure 4, we can easily derive

$$A(\alpha) = A_Z + (A_X - A_Z)\sin^2\alpha \tag{5}$$

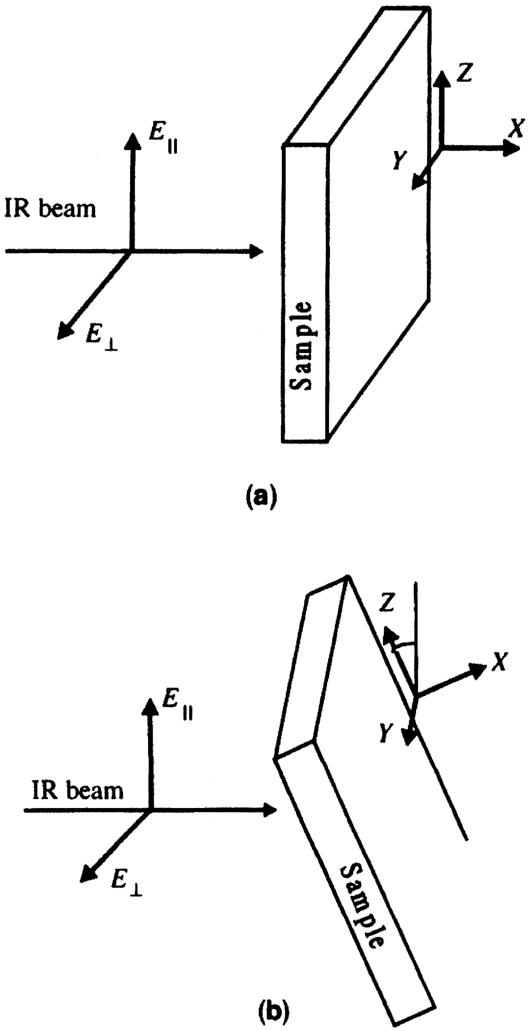

FIGURE 4 Polarized infrared transmission technique at (*a*) normal and (*b*) oblique incidence of light. Sample is tilted by the angle α.

For $\alpha = 90°$, A ($\alpha = 90°$) $= A_X$. In practice the angle α is varied from $-40°$ to $+40°$, knowing A_Z and by fitting the observed $A(\alpha)$ to the angle α, A_X is determined. Results of $A(\alpha)$ as a function of α are given in Figure 5.

The various components of absorbances are related to the order parameter S.

$$A_Y, A_Z = \frac{A}{6}\{2(1 - S) + 3S\sin^2\beta\} \tag{6}$$

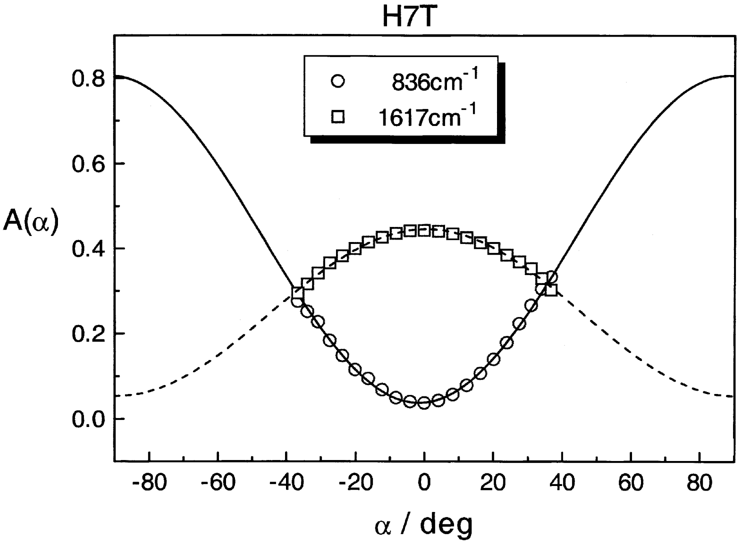

FIGURE 5 Peak intensity dependence vs. the angle a for H7T at the temperature 342 K: (□) C-C aromatic in-plane vibration (1617 cm^{-1}); and (○) C-H aromatic out-of-plane vibration (836 cm^{-1}).

$$A_X = \frac{A}{3}\{2\,S + 1 - 3S\sin^2\beta\}, \tag{7}$$

where $A = A_X + A_Y + A_Z$, is the trace of the absorbance,
β is the angle between the dipole moment and column's axis as in Figure 4a. In order to determine A, its three components must be known. For the transition moments to lie in the plane of the disc $A_Y = A_Z$, however A_X must be determined.

Alignment

The sample of discotic liquid crystal is heated to its isotropic phase on to a Si window, the Mylar film of known thickness used as a spacer is kept on the edges of the window; the second window is placed on the top of the first window. The thickness of the Mylar spacer varies from 6 to 20 μm. The cell so formed is glued around the edges. The cell is slowly cooled from the isotropic phase of the liquid crystalline material to the phases of interest. We find that the discotic liquid crystalline samples of hexa-pentyloxy-triphenylene (H5T), hexa-hexylthiotriphenylene (H6TT) and hexa-heptyloxytriphenylene (H7T) usually self-align to form a homeotropic alignment while the sample is slowly cooled from the isotropic phase. In some cases for homeotropic alignment, it is preferable to spin-coat a film of nylon-6/6 (0.2 to 1% solution in methanol). The windows so spin-coated were first dried for time duration of 1 h at room temperature, and then dried in an oven at 70°C for a period of 24 h. A successful homeotropic alignment was also obtained by spin-coating the windows with poly (amic acid) solution (ZLI 2650) (E. Merck).

For the case of the planar-homogeneous alignment, where the director is parallel to the substrate and pointing in a particular direction, the orientation distribution of the various parts of the molecules can be found from the profile of the absorbance measured as a function of the angle of polarization. The absorbance profile can be fitted using the expression [5,9].

$$A(\omega) = -\log\{10^{-A_\parallel} + (10^{-A_\perp} - 10^{-A_\parallel})\sin^2(\omega - \omega_0)\} \qquad (8)$$

$A_\parallel$ is the maximal absorbance when the polarizer makes an angle of ω_0 with the reference direction. The latter may be the rubbing direction. If this direction is made to coincide with the direction of maximal absorbance, then ω_0 is zero. $A_\perp$ is the absorbance along the direction normal to the direction of maximal absorbance, ω is the angle of polarization of the beam. For these studies, the IR beam is polarized. The absorbance profiles for the edge-on alignment of the discotic H5T on substrates of Si, CaF_2 and ZnSe are shown in Figures 6a and 6b. Large differences in the absorbances on the angle of polarization are observed for the two sets of substrates. For Si and CaF_2 cells, no dichroism is observed. This will be found both in the homeotropic as well as in the planar heterogeneous alignment. In the former the intensity of vibrations in the discotic phase will be greater than in the isotropic phase, whereas the opposite will be true for the edge-on or planar alignment. A pronounced dichroism is observed in the Y-Z plane of a ZnSe cell (Fig. 4b). This implies that the edge-on alignment achieved is heterogeneous. Results of the polarization measurements for cells with ZnS windows are found to be similar to those of the ZnSe windows. The polar absorbance profiles can be used to determine the extent of the heterogeneous planar alignment. In the case of a uniform homeotropic alignment, the dichroism can also be a signature of the biaxiality in the system.

Results on the Order Parameter

The order parameter for the various discotic liquid crystalline materials has been calculated by the methods given above. The calculations are carried out for the various bands. The results for two discotic systems H5T and H7T (chemical names given before) in Figures 7 and 8 are found to be only slightly dependent on the band as the angle of the various band vibrations may not be accurately known. We find that the observed order parameter, close to the discotic-crystalline phase transition, is 0.95 and this slowly

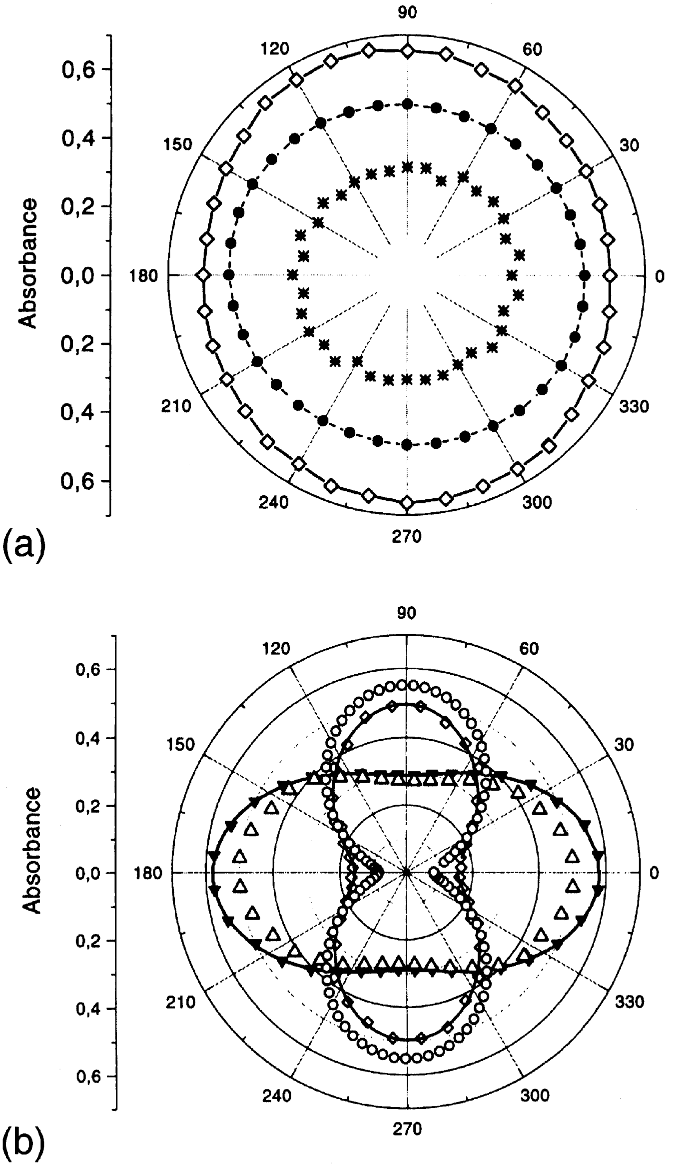

FIGURE 6 The intensity distribution for in-plane (1517 cm^{-1}, 1617 cm^{-1}) and out-of-plane (836 cm^{-1}, 866 cm^{-1}) vibrations in the window plane (Y-Z plane) for (*a*) Si and CaF_2 cells and ●, 1517 cm^{-1} (Si), ◇ 1517 cm^{-1}(CaF2), $*$, 866 cm^{-} (Si) (*b*) for ZnSe cell, ▼, 1517 $cm^{-1;}$ ◇ 866 cm^{-1} experimental, △ 1617 $cm^{-1;}$ ○ 866 cm^{-1} calculated, lines joining the data points on plots (*a*) and (*b*) give the absorbance calculated using Eq. (8).

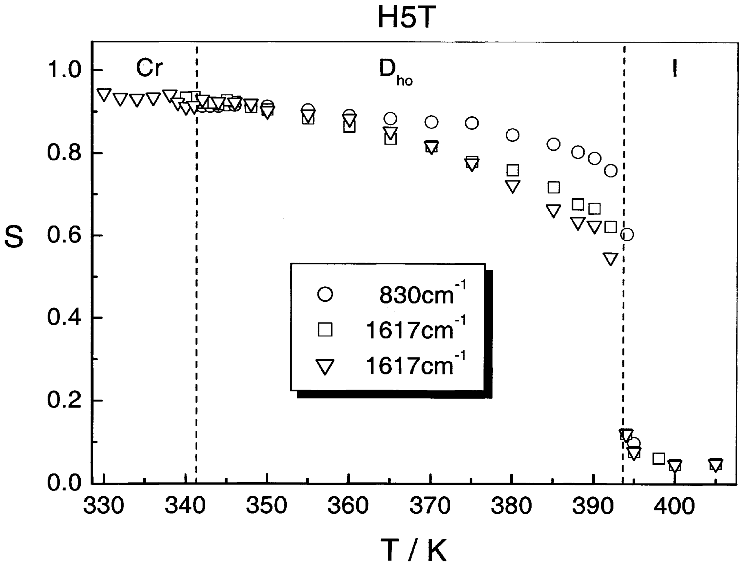

FIGURE 7 Temperature dependence of the order parameter for H5T: (□) on heating and (▽) on cooling for the C-C aromatic in-plane vibration ($1617\,cm^{-1}$); (○) on heating for the C-H aromatic out-of-plane vibration ($830\,cm^{-1}$).

decreases with temperature and reaches 0.7, close to the discotic hexagonal ordered (D_{ho})-isotropic phase transition temperature. S decreases to almost zero in the isotropic phase transition. The transition D_{ho} to I shown is found to be first-order. The results show that discotics, unlike some of the smectic phases, are close to the ordered systems as expected. The results for other discotic systems [11–13] are given in our recent review article [6]. The results for the discotic polymer system are also given elsewhere [14].

Anchoring Transition

We have carried out experiments for alignment of several discotics on a number of different substrates. These are Si, CaF_2, ZnSe and ZnS. The result of our experiments show that if the surfaces are clean, flat within ± 0.1μm, if the material of the substrate is amorphous/isotropic, and the sample is cooled slowly from the isotropic phase, then the alignment achieved for discotics in most cases is homeotropic in the discotic phase. However, if the substrate surfaces are uneven and particularly for the substrate ZnSe, the surface of which is somewhat uneven, has a crystalline structure; the alignment achieved is planar or edge on. Nevertheless, if the sample is cooled to the glassy phase and left at a lower

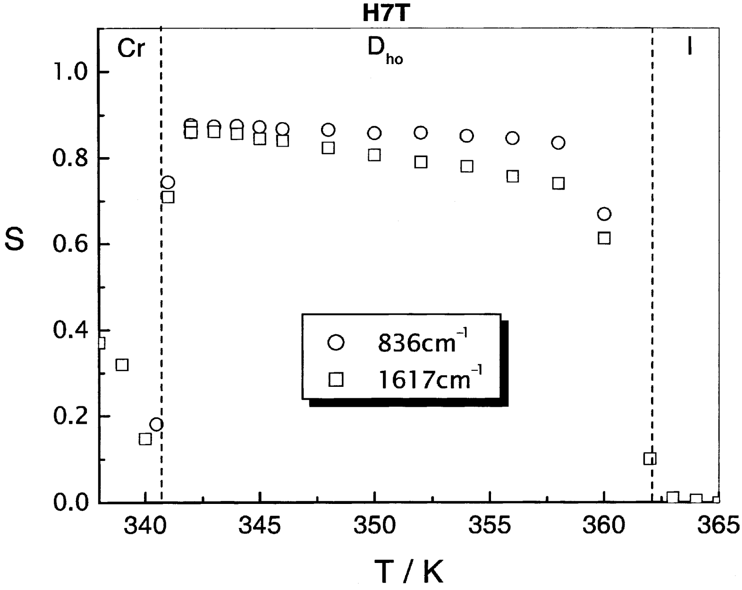

FIGURE 8 Temperature dependence of the order parameter for H7T, substrate Si window (□) C-C aromatic in-plane vibration (1617 cm^{-1}); and (○) C-H aromatic out-of-plane vibration (830 cm^{-1}), on heating. Prior to the measurements, the cell had just been cooled close to the Cr- columnar phase.

temperature for several hours even on a Si substrate, then the alignment changes from homeotropic to planar heterogeneous. In other words, the column's axes get parallel to the surface of the substrate and more or less, these are randomly distributed along the surface. This shows that planar heterogeneous alignment has the lowest energy, especially in the crystalline state. When the sample is slowly heated, the alignment continues to be planar but if the sample is kept for several hours in the discotic phase, then the alignment changes slowly from planar to homeotropic. The time taken by the transition to occur is dependent on the substrate and the temperature at which the sample is kept. Higher is the temperature at which the cell is kept, and more heterogeneous planar is the alignment, less is the time for this change to take place. (Fig. 9). We denote this transition as the anchoring transition, where the column's axis goes from being parallel to the substrate to being normal to it. This implies that the homeotropic transition is thermodynamically more stable. To explain the anchoring transition, the theory of Dubois-Violette and de Gennes [15] applied to nematics is adapted to discotics.

To describe the alignment and the anchoring transition, we need at least 3 terms in the expression for the anchoring energy, one of the

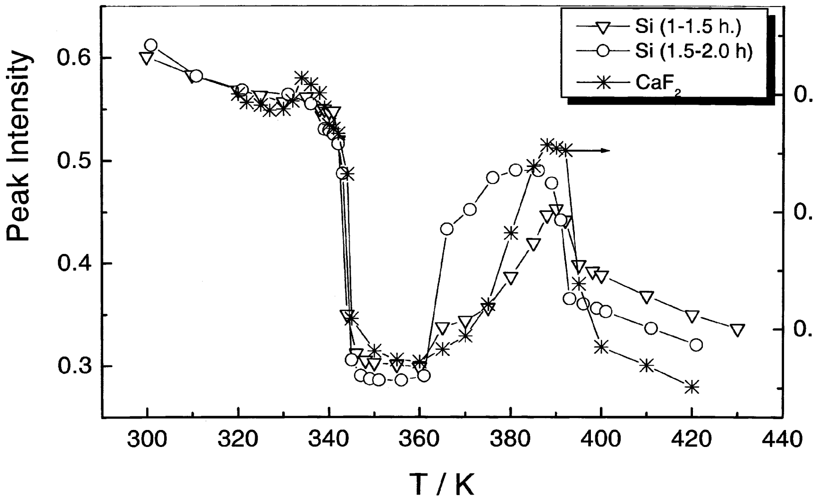

FIGURE 9 The dependence of the peak intensity of C-C aromatic stretching vibration on temperature for H5T in between Si and CaF_2 windows, after a period 1 to 1.5 hours (∇ Si, ∗ CaF_2) and 1.5–2.0 hours for Si windows (O). Note that the sample had been kept in the crystalline/glassy phase for several days and alignment initially achieved was planar heterogeneous (edge-on) while the sample was heated from the crystalline/glassy phase.

terms is connected with the surface anchoring energy. This term must be associated with the short-range interactions between the surface and the discotic molecules. The flatness of the surface and the surface treatment forces the discs to be anchored parallel to the surfaces, and this in turn promotes the homeotropic alignment. The second term must be related to the long-range van der Waals term, this term should promote the planar alignment, where all the discs have a minimum contact with the substrate's surfaces through their edges. The third term must involve the elastic term that should restore whatever order has already been established. When the term due to surface anchoring is weak, the edge-on-alignment or planar alignment is achieved. When the surface anchoring term is strong, or the surface anchoring energy is minimum, the homeotropic alignment is achieved. The details of this discussion are published elsewhere [10].

CONCLUSIONS

We find that the orientational order parameter in most triphenylene based discotic systems (results for H5T, H7T given here) is large and is close to 0.9 in the discotic phase. The order parameter so determined includes the distributions and fluctuations of the angles that the column's axes make and the normal to the individual discs, both with respect to the director. The IR spectroscopy is a convenient and a useful technique for measuring the orientational order parameter. The determination is based on the assumption that the discotic discs are uniaxial, though the analysis can be extended to the discs being biaxial. The observed polar plots of the absorbance profiles indicate that the discotic phase is uniaxial. Topology of the surface determines the type of alignment. We determine the requirements of the homeotropic or side-on alignment. The substrate should be flat and isotropic/amorphous such as glass and Si. The substrate should preferably be spin-coated with a polymer solution with a layer of thickness varying from $\sim$ 0.03 μm 0.1 μm. The latter thickness is preferred. The solutions used for spin-coating the substrates are 1 to 2% solution of nylon 6/6 in methanol and 1% solution of poly vinyl alcohol in ethanol. The layer is cured at a temperature of 70°C for 24 hours in order that this is polymerised. The sample is slowly cooled from the isotropic to the discotic phase. The anchoring transition from planar to homeotropic alignment is usually observed on heating the sample and bringing it close to the isotropic temperature. The observed phenomenon is opposite to that reported by Shimizu [16] where by shining the IR laser on to the aligned discotic, they found that the IR heating affects the alignment: columns from being normal to the substrate fall down and these become parallel to the substrate's surface. It is also found that the edge-on alignment has a lower energy especially in the crystalline phase. The fluctuations arising from the thermal energy drive the transition as the side-on alignment is found to be thermodynamically more stable. The polar plots of the absorbance profiles for the side-on alignment indicate that the discotic phase is uniaxial.

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