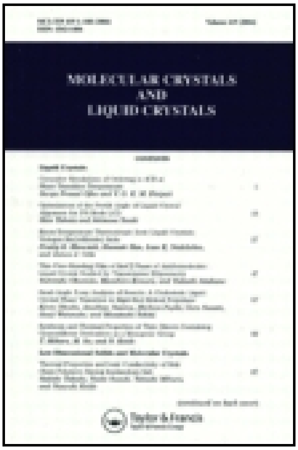

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Lyo-Mesophases from Self-Assembled Disk-Shaped Molecules

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We report the self-assembly of disk-shaped molecules that from lyotropic nematic and cholesteric phases in triphenylene-based thermotropic discotic liquid crystalline compounds. A discotic nematic monomer, which exhibits nematic melt at 103°C and isotropization temperature at 180°C, showed room-temperature nematic phase when dissolved in suitable organic solvents at an appropriate concentration. In case of a discotic cholesteric monomer, whose clearing temperature is 190°C, showed cholesteric phase at room temperature cholesteric lyo-mesophase 55 wt% in xylene. The lyo-mesophases of discotic materials, when filled in LC cells, were electrohydrodynamically switchable. We obtained discotic cholesteric films with selective reflected color from an aligned and polymerized cholesteric lyo-discotic system. The temperature dependence of reflection of cholesteric lyo-discotic system was also determined.

Keywords: self-assembly; discotic liquid-crystals; lyotropic; photopolymerization

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1. Lyotropic phase study

In addition to their popular applications in electro-optical display devices, liquid crystals have become increasing important for optical filters and directed energy control devices.[1,2] Liquid crystals having a discotic cholesteric phase, in principle, can exhibit flexoelectricity. Although discotic liquid crystals have potential for applications, there are a number of hurdles to be overcome before their full usefulness of discotic materials can be realized, such as high phase transition temperature and alignment problems. In addition, much more materials development and characterization are needed. It was shown recently that lyotropic liquid crystal phases could be obtained by dissolving thermotropic liquid crystals in suitable organic solvents.[4-6]

In our previous study on discotic molecules,[7] the epoxy monomer (Fig.1) showed thermotropic behavior with crystalline to nematic transition at 103°C and nematic to isotropic transition at 170°C. Similarly chiral monomers exhibited thermotropic characteristic with C1---C2 (or C—discotic) at 150°C, C2 (or discotic)---cholesteric at 190°C and cholesteric---isotropic transition at 220°C. Just before isotropization it also showed characteristic blue phase of cholesterics. This blue phase is also observed on cooling from isotropic state. A mixture of epoxy and chiral monomer (with chiral monomer concentration above 2 weight %) also shows cholesteric mesophase above 100°C and blue phase near the isotropic state (170°C), similar to pure cholesteric monomer. Further, study of such mixture in suitably prepared wedge cell also revealed the Cano-Grandjean lines, oily streaks and fingerprint texture common of cholesterics.

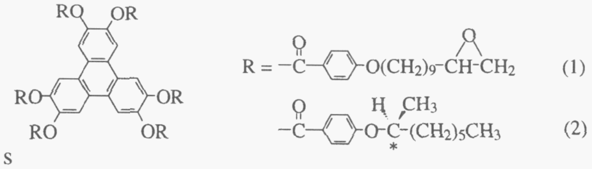

Figure 1. Discotic nematic epoxy and chiral dopant.

Interestingly both above compounds also exhibited lyotropic mesophase at room temperature in solvents such as xylene, alkyl benzene, benzyl trimethyl silane, etc., as well as 1,3-dichlorobenzene when concentration of monomer was greater than 60 weight percent. Below this concentration, it remained in the isotropic phase. In addition to fingerprint and Grandjean textures, characteristic blue reflected color is also observed in mixtures of both monomers prepared in one of the solvents. The results of lyo-mesophases study formed from self-assembled disk-shaped molecules are summarized in Table 1.

Table 1: Lyotropic study of disk-shaped molecules at room temperature

Sample	Solvent	POM Texture at RT
Epoxy nematic monomer (**1**)	Xylene/1,3-dichlorobenzene	Nematic Schlieren texture (Fig 2a, 2b)
(**1**)	Benzyl trimethyl silane	Nematic threaded texture (Fig. 2c)
Cholesteric compound (**2**)	Xylene/ 1,3-dichlorobenzene	Chloesteric blue phase (Fig 2d)
(**1**)+ 2% (**2**)	Xylene	fingerprint texture (Fig. 2e)
(**1**) + 5% (**2**)	Xylene	Fingerprint texture
(**1**) + 10% (**2**)	Xylene	Fingerprint texture (Fig. 2f)
(**1**) + 40% (**2**)	Xylene	Distinct blue color reflection (Fig. 2g)

(RT = room temperature) (concentration: sample/solvent = 1:1 weight %).

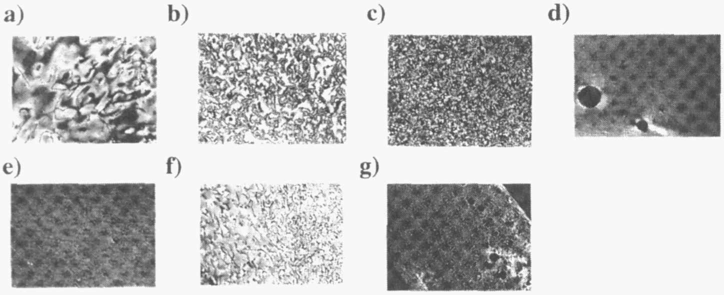

Figure 2. (a) Marble nematic texture of (**1**) in 45 wt% xylene; (b) Nematic schlieren texture of (**1**) in 45 wt% 1,3-dichlorobenzene; (c) Threaded nematic texture of (**1**) in 45 wt% benzyl trimethyl silane; (d) Blue reflected color of pure (**2**) in xylene; (e) Mixture of (**1**) and 2 wt.% of (**2**)in 45 wt% xylene; (f) Mixture of (**1**) and 10 wt.% of (**2**)in 45 wt% xylene; (g) Blue reflected color of mixture of (**1**) and (**2**) (60/40) in 45 wt% xylene.

2. Response of lyo-discotic materials to applied electric field

The lyo-discotic solutions were filled in 5 μm cell gap homeotropic E.H.C capillary filling cells. To overcome the solvent evaporation problem, cells were successfully filled in a solvent chamber of xylene (to keep constant solvent vapor pressure). In this way, cells were filled under saturated vapors of xylene, thus minimizing xylene evapoation from the mixture. Cells with pure epoxy monomer (Fig 3a) and mixtures of epoxy and chiral (90:10, 70:30 and 50:50) (Figures 3b-3d) were prepared in the same manner. The cells were sealed using epoxy glue, and electric wires were soldered for applying electric field to the cells. Results of response of lyo-discotic materials to applied electric field are tabulated in Table 2. For all cells, electrohydrodynamic switching was observed[8] between bright and dark states above a critical voltage and at lower frequency (1Hz). When low weight ratio (<10%) of chiral monomer was present fingerprint texture wsa observed above characteristic voltage (5.3) at low frequency (1Hz). However, at higher frequency (1kHz) but keeping same voltage, it switched to homeotropic similar to pure non-chiral epoxy monomer. For higher chiral concentration (30 and above) samples, fingerprint texture stood change at lower voltage (< 10 volts) even with higher frequency (1kHz). With further increase in voltage (11.25 V for 30 wt. % chiral and 18.0 V for 50 wt. % chiral), it again switched to homeotropic at higher frequency (1kHz). Detail electro-optical properties of lyo-discotic systems will be studied in the future.

Table 2. Response of lyo-discotic materials to applied electric field.

No.	**Composition (1) : (2) (wt. %)**	**Applied Voltage (V)**	**Frequency (Hz)**	**POM texture**
1	100: 0	8.5	1	Switching
2	90:10	7.5	1K	Fingerprint texture (Fig. 3b)
3	70:30	11.25	1K	Homeotropic
4	50: 50	9.3	1	Switching
5	50:50	9.3	1K	Fingerprint texture (Fig. 3c)
6	50:50	18	1K	Focal conic texture (Fig. 3d)

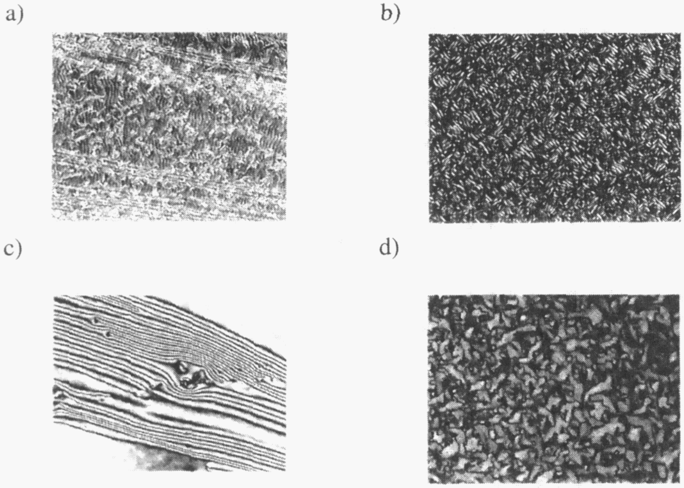

Figure 3. Photomicrographs of lyotropic cells a) (**1**) + 45 wt% xylene in 5 μ homeotropic EHC cell (no electric field); b) Finger print texture: (**1**): (**2**) = 70: 30 in 45 wt% xylene (5 μ homeotropic EHC cell, 7.5v, 1KHz); c) Finger print texture: (**1**): (**2**) = 50: 50 in 45 wt% xylene (5 μ homeotropic EHC cell, 9.3v, 1KHz); d) Disappearance of fingerprint texture at high voltage: (**1**): (**2**) = 50: 50 in 45 wt% xylene (5 μ homeotropic EHC cell, 15v, 1KHz)

3. Fluorescence study of lyo-discotic materials

Emission and excitation spectra of various solutions in xylene (isotropic, nematic and cholesteric) are presented in Figure 4. For isotropic solution, the emission peak appeared at 419 nm when excited at 378 nm. Both excitation and emission peak were mirror images. In nematic solution (concentration of epoxy in xylene 60 wt%) again similar excitation and emission peaks at 378 and 419 nm, were observed respectively. However, the excitation and emission peaks were not mirror images. Emission peak intensity was much higher than excitation. This can be explained as emission from liquid crystalline aggregates, i.e., in liquid crystalline state number of molecules (or associated molecules in liquid crystalline phase) emitting at 419 nm is much higher than in the isotropic state, giving rise to highly intense emission as compared to excitation. Similar results were also observed for the chiral sample with

50:50 epoxy and chiral monomer in xylene. In addition, little shift to blue region was observed with excitation at 372 nm and emission at 414 nm.

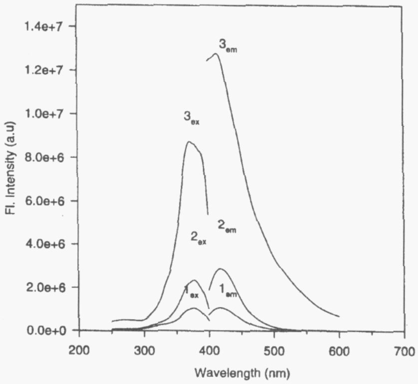

Figure 4. Fluorescence studies of lyo-discotic systems: 1em and 1ex (excitation and emission of isotropic sample); 2em and 2ex (lyo-discotic nematic sample); 3em and 3ex (lyo-discotic cholesteric sample of 50% chiral dopant).

4. Reflection properties of cholesteric lyo-discotic films

Thin films of cholesteric lyo-discotic materials, with chiral concentration of 20 and above, reflect orange to blue color with films cast on glass plates as well as on glass plates coated with polyimide alignment substrates. Reflectivity of reflected colors was determined using an integrated sphere attached spectromer. Thin cholesteric lyo-discotic films show characteristic reflection wavelength between 400-500 nm at room temperature. The reflected band shifted to longer wavelength for consecutive scans (Fig 5a) because of heating of the specimen i.e., change of cholesteric pitch with temperature increase in thesample measurement chamber. To fix a reflected color photopolymerization was carried out with a mixture composed of 70 wt% epoxy, 30 wt% chiral and 2 wt% (based on epoxy monomer) catalyst Irgacure 261 in 45 wt% xylene. This mixture was cast (either spin coating or roller coating) on glass plates or ITO glass plates coated with rubbed PI alignment layer. The cast film was sandwiched using another plate with rubbed PI alignment layer. The cell was assembled with the rubbing direction in an anti-parallel position and sealed with epoxy glue. The sample was then polymerized by UV radiation (intensity = 1 mW/cm^2) for 30 minutes at room temperature and at elevated temperatures (30, 40 and 50ºC). After polymerization color was fixed in, namely, blue (at 20ºC), blue-green (30ºC), green-yellow (40ºC) and orange (50ºC). Once the sample was polymerized, the reflection colors (cholesteric pitch) became temperature independent because of the highly crosslinked network. Figure 5b shows reflectance of regions of specimen before polymerization at room temperature, after polymerization at ambient and high temperature. Before polymerization, the maximum of a reflection band appears at 470 nm at room temperature with intensity 23.7%. After polymerization at room temperature the peak remained globally at the same position, i.e., with peak at 470 nm but with somewhat reduced intensity, 22.4 %. Further, when it was polymerized at 50ºC, the peak shifted to 627 nm with intensity 21.8% (Fig. 5b). Orange color can also be observed visually for this region of the specimen. A photo of a cholesteric lyo-discotic film reflecting blue, green and orange colors, prepared by masked photopolymerization, is shown in Fig. 6.

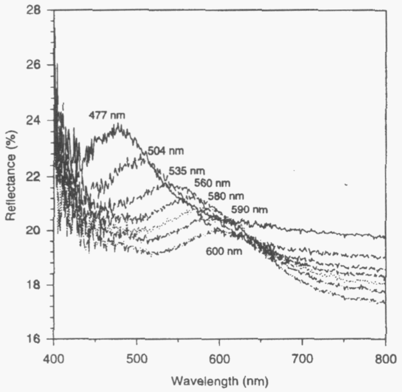

Figure 5 (a) Temperature dependence of reflection spectra of thin films of cholesteric lyo-discotic materials.

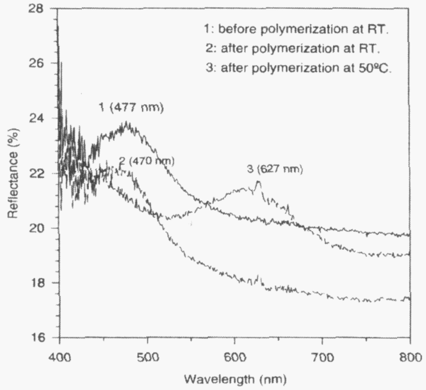

Figure 5b. Reflection spectra of thin films of photo- polymerized chiral (30 wt%) lyo-discotic material (55% in xylene) at R.T. and 50°C.

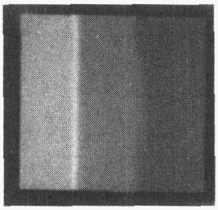

Figure 6. A cholesteric lyo-discotic film with selected reflected colors on a black absorbing layer was prepared by masked photopolymerization. See Color Plate VIII at the back of this issue.

CONCLUSIONS

We succeeded in preparing discotic nematic and cholesteric lyotropic systems from thermotropic discotic liquid crystals whose phases were observed over a wide temperature range and down to room temperature. Both the nematic and cholesteric lyo-discotic systems were electrohydrodynamically swithcable. Using a short pitch cholesteric lyo-discotic, we prepared thin films with patterned colors.

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