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Synthesis and Degradation Studies of Nematic (N^*) Liquid Crystals

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Abstract

Cholesteric Liquid Crystals (LCs) are synthesized and characterized for their optical properties. The optical properties of cholesteric LCs have been investigated with varying applied field and time. The electric field is applied in the range of 0V – 13V, whereas time is varied between a few seconds and 95 minutes. These cholesteric LCs are aged at room temperature as well as at higher temperatures up to 70^{o}C. Degradation of these cholesteric LCs under different conditions is also reported in this paper. Multi-step purification process was carried out and both the filtrate & residues are analyzed for phase identification. XRD analysis confirms the presence and absence of the main ingredients in the solution as well as in the residue.

Introduction

Liquid crystals (LCs) are anisotropic fluids, thermodynamically located between the isotropic liquid and the three-dimensional positional ordered solid phase. Due to molecular self-assembly LCs exhibit orientational order of rod-shaped molecules, i.e., anisotropic physical properties, while at the same time maintaining flow properties in their least ordered configuration, the nematic phase [Figure 1]. The direction of the average long molecular axis of a nematic liquid crystal, called the director n, can be easily controlled by suitable alignment layers. In addition, the director can be reoriented by the application of electric or magnetic fields exploited in all common LCD applications from cheap wrist watches to the highly sophisticated laptop displays [1-3].

Figure 1: Nematic phase of liquid crystals

Liquid crystals of rod-shaped molecules show mesoscopic chirality when they contain chiral molecules such as cholesteryl derivatives. These materials usually form a chiral nematic N* phase, which possesses helical structures with the pitch ranging from sub micrometers to hundreds of micrometers [1, 4]. In addition to the chiral nematic phase, chiral liquid crystals may also form smectic and twisted grain boundary phases. Smectic phase exhibits helical structures only if the director is tilted with respect to the smectic layers e.g., the chiral smectic C* or SmC* phase [5].

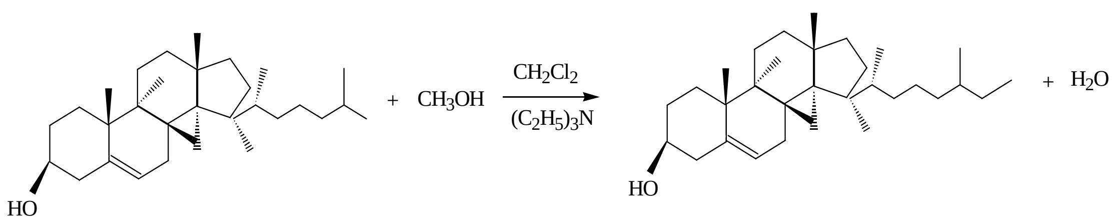
The periodic helical structure of cholesteric liquid crystal is changed by stimuli like temperature, electric fields and impurities [1, 4, 6]. Therefore, if there is a system to enable the periodic helical structure of the cholesteric molecules [7] to be changed and fixed reversibly, it is possible to apply it to the full-colour rewritable recording, which shows different colours with single type molecule or single composition [8, 9]. These cholesteric-nematic liquid crystals reversibly change color as the temperature changes [10]. Thus, one of the principal advantages of such liquid crystals is their ability to map out thermal regions of different temperatures. Cholesteric LCs can degrade when exposed to moisture or air [11], but as long as they are stored in a sealed container the mixture can be prepared months in advance. Early color-related uses of cholesteric LCs were in temperature dependent applications. By the 1970's [1], cholesteric LCs had become durable and colorfast [12] enough to appear in consumer products like thermometer strips, inks, and ever fashionable mood rings. But, cholesteric LCs remain highly sensitive to chemical solvents [13], and more robust approaches are needed to create commercial cholesteric LC systems.

In this paper, synthesis, thermal degradation and stability of cholesteric liquid crystals based on (35, 85, 95, 10R, 13R, 14S, 17R) – 10, 13-dimethyl – 17 – [(2R) – 6 – methyl heptane – 2 – yl] compound are reported. Transmission through the solution is considered to be an indicator of molecular orientation. The reduction in transmission under different experimental conditions is correlated to the quality of synthesized nematic (cholesteric) liquid crystals.

Experimental Details

Synthesis

Cholesterol based liquid crystals were synthesized with locally available raw materials. Pre-determined ratios of methanol, hydrochloric acid, cholesterol and triethylamine were mixed in flask placed in an ice bath. Another solution was prepared by mixing methanol into hydrochloric acid. Mixing rate was controlled up to one drop per 5 seconds. When the second solution was completely mixed, flask was taken away from the ice bath. This mixed solution was kept at room temperature overnight. The chemical structure of the resultant product (35, 85, 95, 10R, 13R, 14S, 17R) – 10, 13-dimethyl – 17 – [(2R) – 6 – methyl octane – 2 – yl] is given below:



Purification

The resultant solution was purified by a two step purification process. In the first step, solution was passed through a filter paper to separate out residues while in the second step de-ionized water was added to the synthesized solution in order to remove the inorganic constituents of the liquid crystal solution. This solution was mixed and shaken thoroughly till two different layers of dissolved inorganic portion, in water, and un-dissolved organic portion were observed. The organic layer was extracted from the lower tap of the funnel. Rest of the solution was re-shaken to ensure the extraction of all organic part from the solution. At the end of this process, the amount of water present in the extracted organic solution was removed by passing the solution through magnesium sulfate. The purified liquid crystal was acidic in behaviour so it was neutralized by adding base triethylamine [$(C_2H_5)_3N$].

Polymerization

To observe polymerization effects in the liquid crystals one drop of the synthesized solution was poured onto a glass slide and was examined under an optical microscope after aging at room temperature and after heating to a maximum temperature of 70^{o}C. In the polymerization process mesogens grow to form molecules, and molecules get linked into chains. The chained network extends throughout the liquid as can be seen in the optical micrographs (as shown in the results & discussions section).

Characterization

Synthesized liquid crystals were characterized in different ways to ensure the phase formation and the rod like structure. Surface morphology and polymerization at different temperatures was observed using Leica DM-400 metallurgical optical microscope. Rotation of the optical axis was observed by applying dc electric field in the range 0V - 13V with the liquid placed in the sample compartment of Shimadzu UV-240 spectrophotometer. The main features of this spectrophotometer are:

Wavelength range:	190 – 900 nm
Stray light:	0.05%
Spectral resolution:	0.15 nm

Rigaku D/Max-IIA x-ray diffractometer was used, under the conditions given below, to verify the compounds.

X-ray	Cu K_α (Ni filtered)
Wavelength	1.5405 Å
Tube Voltage	35 kV
Tube Current	25 mA
Angular Range	$5^o – 80^o$ (2θ)
Step Width	0.02^o (2θ)
Preset Time	0.4 sec
Detector	Scintillation Counter

Results and Discussions

The synthesized & purified liquid crystal solutions were checked for their physical properties. In order to confirm the presence of cholesterol in the purified LC solutions XRD technique was used as discussed above. The X-ray diffractogram of Figure 2 shows cholesterol peaks (except for one) as confirmed by JCPDS Card No. 7-740. Figure 3 shows the XRD trace of the filtrate showing absence of cholesterol.

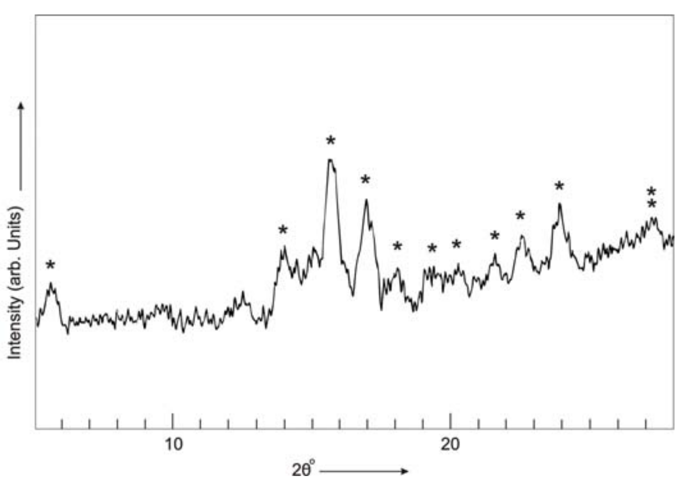


Figure 2: XRD trace of purified LC solution showing peaks of *Cholesterol, **3-Phenyl 1-Propyl, 3,5 dinitrobenzolate

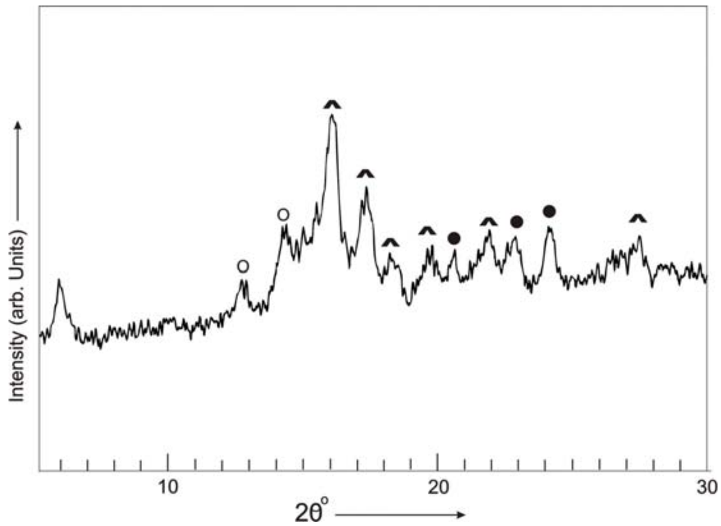


Figure 3: XRD trace of residue showing peaks of ^Methyl pregnene dione, •Benzimidazole hydrochloride hydrate, °Phenylephrine hydro chloride

Optical microscopy was used to observe structure and thermal degradation in these cholesterol based nematic LC solutions. The solutions were treated at different temperatures in order to see the changes in the properties of these liquid crystals. Rod like molecules with different orientations, as expected for nematic chiral liquid crystals were observed as shown in Figure 4 [14].

Figure 4: Optical micrograph at 50X magnification of as-prepared LC solution

After aging for 24 hours at room temperature, rod like molecules started to merge into each other [Figure 5]. To observe detailed effect of time these crystals were aged for one week and almost all chains broke down, which converted into groups of molecules rather than the networks of chains [Figure 6].

Figure 5: Optical micrograph at 50X magnification of 24-hrs aged LC solution

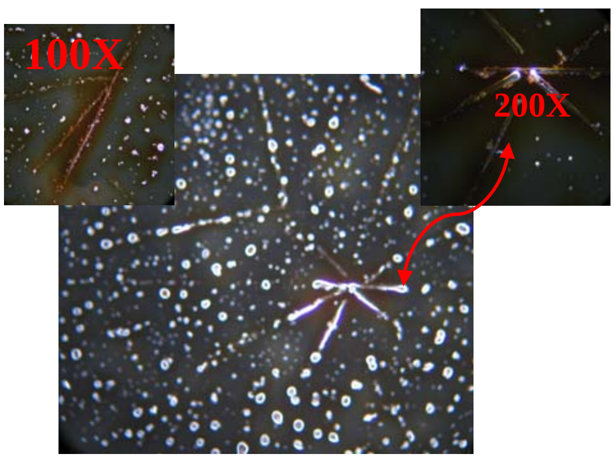


Figure 6: Optical micrographs of one-week aged LC solution

To check the aging effects with temperature a sample was heated using the heating stage of Leica Optical Microscope. In Figure 7, optical micrograph is shown for a sample heated at a temperature of 50^{o}C. Remarkable changes in the colour and merging of branched network is observed. These changes continued when the temperature was raised to 60^{o}C [Figure 8]. Cholesteric liquid crystals contain mixtures of molecules that align in layers. Stacks of layers are rotated with respect to one another similar to DNA, spiral staircases, or screw threads. The rotation between layers increases with temperature. A color will be reflected when the pitch, the distance between layers that have the same orientation, is approximately equal to the color's wavelength of light. Since the pitch changes with temperature, the color changes with temperature [15-18]. A complete thermal degradation of these liquid crystals was observed at a temperature of 70^{o}C [Figure 9].

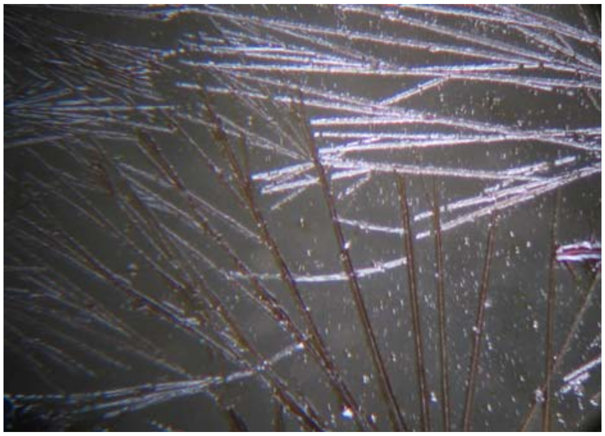


Figure 7: Optical micrograph at 50X magnification of LC solution heated at 50^oC

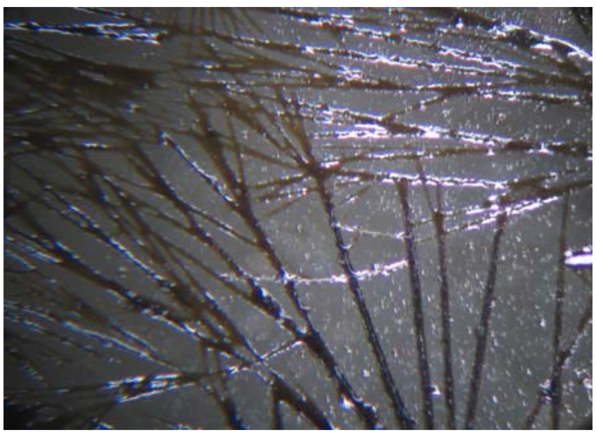


Figure 8: Optical micrograph at 50X magnification of LC solution heated at 60^oC

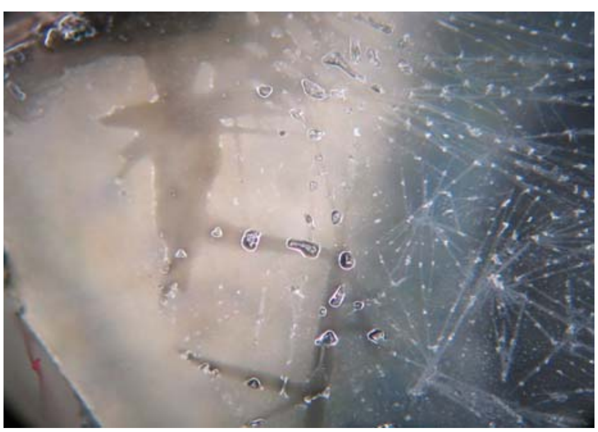


Figure 9: Optical micrograph at 50X magnification of LC solution heated at 70^oC

This thermal degradation can be correlated to the chemical changes that are given in Figure 10, as discussed by Meijer et al [19]. The thermal degradation was correlated to oxidation of cholesterol [19] thus changing the character of liquid crystals. These samples were also checked for degradation under applied voltage conditions, as discussed below.

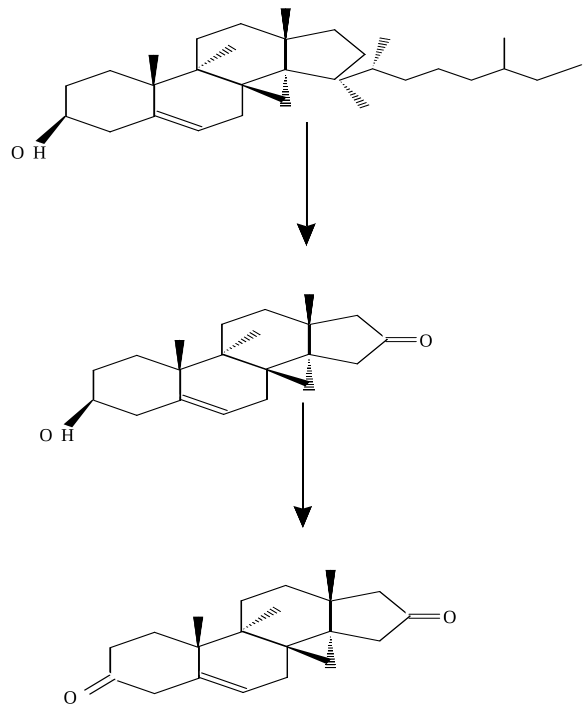


Figure 10: Representation of structural degradation showing changes in the chained structure leading to the loss of hydoxyl group

These LC solutions were tested under different voltage values (0 – 13V) coupled with electromagnetic radiations in the range of 300 – 900 nm. It was observed for as prepared LC solution that in the absence of electric field almost 80% of the incident radiations transmitted through as shown in Figure 11. This figure shows a sudden decrease in transmission around 450nm, with a small peak around 350nm. A systematic decrease in transmission was observed with every change in the applied field; once again shown in Figure 11. Further, the small peak at 350nm in transmission is correlated to rotation of the crystals. The presence of two peaks is speculated to be because of different pitch lengths present in this LC solution. This can be supported by the fact that this short-wavelength peak disappears at higher voltages [Fig. 11] and at higher temperatures [Figs. 13 & 14] possibly because of the destruction / merger of various crystals as shown in the optical micrographs.

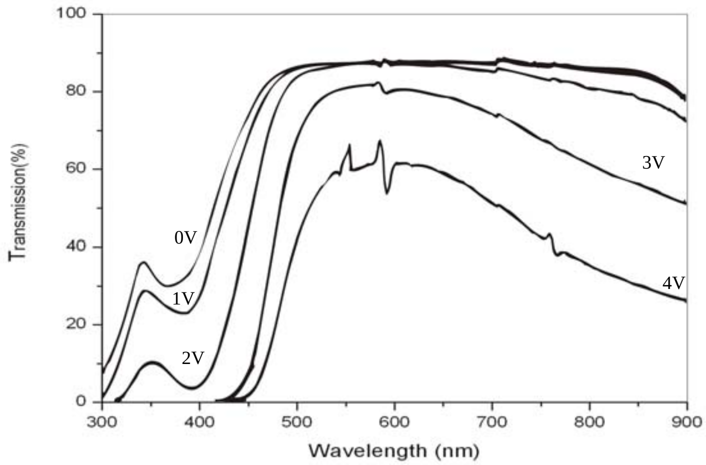


Figure 11: Transmission plots for as-prepared LC solution

Remarkable reduction in transmission was observed at an applied voltage of 4V. Further decrease in transmission was not observed and the liquid crystal solution degraded beyond 4V when a large current started flowing, which not only limited the applied voltage but changed the color of the solution to a very dark murky hue. The optical properties could not be recovered after the change in experimental conditions. The purified solutions were then tested for transmission. In this case, the applied voltage was fixed to a moderate value of 1.65 V and change in transmission was recorded with time as shown in Figure 12. These plots give almost zero transmission value after 53 minutes, which shows that majority of the crystals are now oriented perpendicular to the light path. The pitch of these cholesterol based nematic liquid crystals is estimated to be in the range of 0.58 – 0.60 µm.

Liquid crystal solution heated to a temperature of 50°C was then checked for the transmission. Once again, maximum transmission was observed when no voltage was applied. The transmission decreased drastically by increasing the voltage up to 1.65V. The applied voltage was fixed at this value and change in transmission was then recorded with time. The resultant transmission plots are shown in Figure 13, which gives minimum value after 95 minutes. However, this time near zero transmission was not seen even beyond 95 minutes of applied potential.

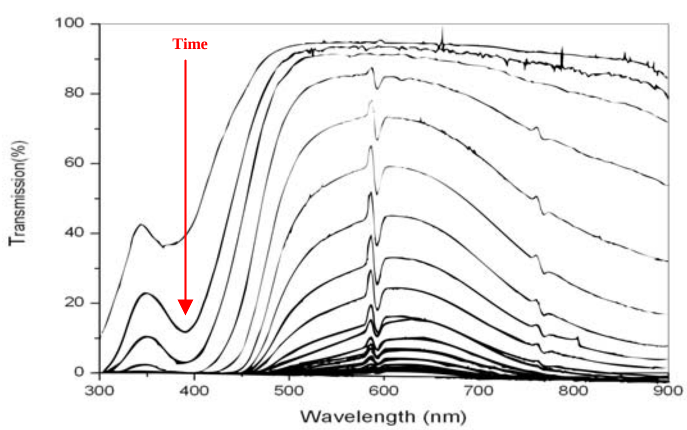


Figure 12: Transmission plots for purified LC solution

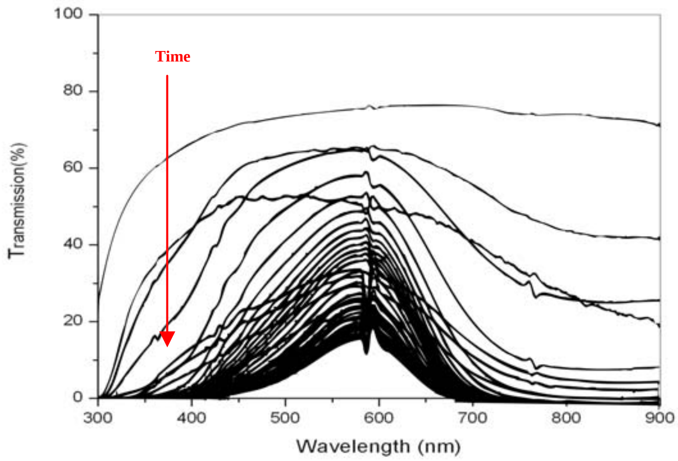


Figure 13: Transmission plots for LC solution heated at 50°C

Next, the liquid crystal solution heated at 60°C was tested for changes in transmission with the applied field. Same trend in the transmission values was observed as discussed earlier, which is shown in Figure 14. For this heated solution, the minimum value of transmission was higher than the previous two cases. These results for as-synthesized & purified LC solutions indicate that the reflection property improved with purification while it degraded with heating to a temperature of 50 – 60°C. Distribution of filament is temperature dependent as can be seen from Figures 7, 8 and 9. At relatively lower temperatures the molecules or the layers of liquid crystal molecules are closely spaced and aligned almost parallel to each other but when temperature is increased not only the distance between the filaments increases the relative angle of the adjacent layers also changes [20].

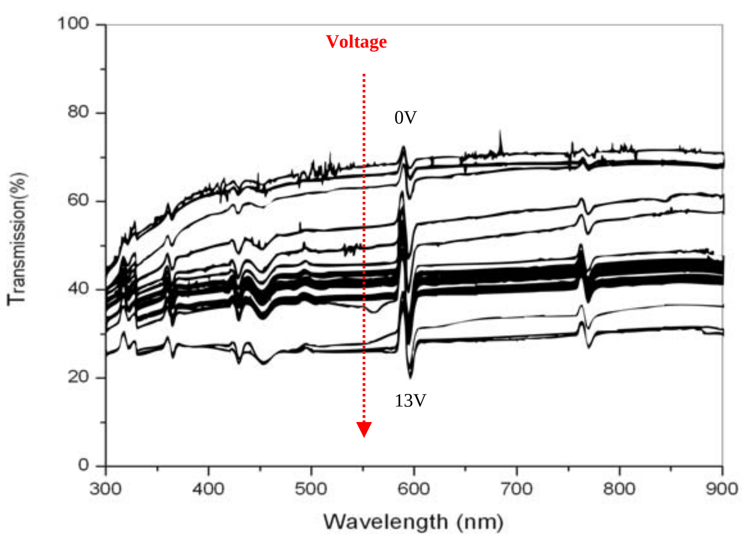


Figure 14: Transmission plots for LC solution heated at 60°C

Conclusions

In summary, the transmission through nematic liquid crystal solutions has been used as an indicator for observation of rod like molecular growth and orientation of these under the applied conditions. The purified cholesteric liquid crystals showed that near zero transmission at an applied potential of 1.65V was achieved, indicating rotation of the rod like molecules. Optical microscopy confirmed rod like structure of the molecules of these cholesteric liquid crystals. These results have been correlated to the synthesis and other conditions of the solution. Degradation in the quality of these nematic liquid crystals was also studied and the results have shown that these structures degraded with time under various applied voltages, at room temperature, and with change in temperature with a maximum withstanding temperature of 60^{o}C.

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