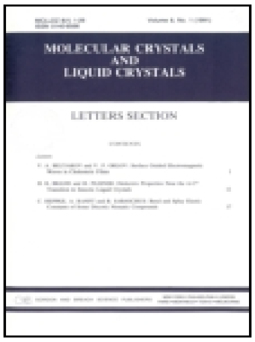
MOLECULAR CRYSTALS
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LETTERS SECTION

Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

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To cite this article: Dharmendra Pratap Singh, Tripti Vimal, Swadesh Kumar Gupta, Prachi Tripathi, M. C. Varia, Sandeep Kumar, Shashwati Manohar & Rajiv Manohar (2016) Tailoring of cholesteric plane spacing, dielectric relaxation and optical properties of high temperature chiral nematic phase by UV irradiation, Molecular Crystals and Liquid Crystals, 625:1, 1-10, DOI: 10.1080/15421406.2015.1044714

To link to this article: http://dx.doi.org/10.1080/15421406.2015.1044714

MOL. CRYST. LIQ. CRYST.
2016, VOL. 625, 1–10
http://dx.doi.org/10.1080/15421406.2015.1044714

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Tailoring of cholesteric plane spacing, dielectric relaxation and optical properties of high temperature chiral nematic phase by UV irradiation

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ABSTRACT
The effect of Ultra Violet (UV) irradiation on the high temperature chiral nematic (N*) mesophase has been investigated. The controlled UV exposure produced bending in rod shape molecules. The bending of molecules affects their long molecular axis; therefore, the relaxation mode associated with the rotation of molecules along the long molecular axis shifts toward the higher frequency. The UV irradiation also increases the cholesteric plane spacing of N*LC molecules. The a.c. conductivity of N*LC has been increased enormously after UV irradiation. The efficiency of opto-dielectric effect has also been evaluated with the variation of bias voltage in the present investigation.

KEYWORDS
Conductivity; dielectric property; optical property.

Introduction

The influence of high energetic radiation on soft materials like liquid crystals (LCs) induces some salient features in the material. The photoinduced phenomenon evolves molecular ordering or disordering in soft condensed materials. The field of LC research has attracted a great interest of researchers and industry due to its self-assembling nature, electric field driven properties and light dependent mechanism [1–3]. In LCs, the physical properties can be altered by the influence of external electric field, photo induction and doping them by mesogenic or non-mesogenic material. The use of photoinduction in LCs is a present perspective for the technology of information processing and optical storage devices [4, 5].

The effect of photoinduction on the LC matrix can takes place in the form of structural transformation of the matrix, orientational alteration of the molecules or reversible/irreversible changes in the properties of LC. Therefore, the photoresponsive liquid crystals (PRLCs) provide promising photofunctional materials for photogenerated devices. Photo-optical effects in LC systems are produced by the induction of photo driven changes in the alignment of LC molecules [6]. The effect of photochemical process on the properties of chiral nematic LCs has scarcely been studied. The first report on the change in cholesteric

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pitch of a mixture of cholesteric iodide and cholesteric nonanoate due to the photodecomposition of the iodide has been reported by Haase et al. [7]. In this study, the reflection wavelength of chiral nematic LC was manipulated by the photodegradation of chiral groups. Photochemically induced reversible colour changes in cholesteric LC has also been reported by Sackman [8]. Some other research groups [9, 10] have developed a special photochemical isomerization reaction to influence the chirality of the compounds. Yarmolenko and co-workers [11] have studied the influence of photoisomerization process on the pitch of the chiral menthone derivatives dissolved in LCs. The photochemical modification in spontaneous polarization of a FLC material has also received some interest [12] whereas Prasad et al. [13] has reported the photoinduced N-I phase transition in the LC system. The change in transmittance of incident light of a LC material irradiated by UV light is also an example of the skeleton of photo application for LC systems [14].

During the last decade, the advent application of photoinduction is to use this method as photo alignment for the LC system in the presence of a photoactive material [15–18]. Photoisomerization in the photoactive materials takes place under the influence of UV radiation; therefore, the formation of cis and trans isomers of materials produces some basic changes in the molecular arrangement. Due to these changes, some physical parameters of the materials are also altered as reported in the literature [19].

In the present study, we report the effects of photo-irradiation on a high temperature N*LC. The UV irradiation on the N*LC causes the bending in rod shape molecules. The UV irradiation changes the cholesteric plane spacing which leads the higher pitch value. The change in pitch has also been supported by the polarizing optical micrographs which shows the change in reflection colour of the N*LC after UV irradiation. The a.c. conductivity of N*LC irradiated by UV light has been changed remarkably. The UV irradiation changes the geometrical shape of N* LC molecule, therefore, the relaxation mode due to the rotation of long molecular axis shifts towards the higher frequency side. It is found that the influence of photoinduction on the physical properties of N*LC is irreversible in nature. The present investigation deals with the photoinduced effects in N*LC without a guest photoactive material however the various research groups have reported the photoinduced changes in the absence or presence of a guest photoactive material [20, 21]. The change in geometrical shape, polarizing optical micrographs, a. c. conductivity, dielectric relaxation and opto-dielectric efficiency of the pristine N*LC due to UV irradiation has been discussed within the scope of this paper.

Experimental

N*LC sample and instruments used

The chiral nematic liquid crystal (N*LC), used in the present study, is 2-(cholesterol-n-decanoate)-6-(heptyloxy benzoate) naphthalene. The transition scheme of N*LC is Isotropic-228.65°C- N*LC- 139°C- Crystal. The detailed information about the synthesis and characterization of the N*LC has been reported recently by Singh et al. [22]. The molecular structure of N*LC is shown in Fig. 1.

The experimental arrangement used in the present investigation is depicted in Fig. 2. The UV radiation was exposed on the N*LC material, mounted on a hot plate (INSTEC HCS-302 USA), by a UV lamp of medium pressure and low power (15 mW/cm^2). The desired bias voltage for opto-dielectric measurement was applied by a function generator (TEKTRONIX AFG 3021B) whereas the dielectric measurements have been performed by Impedance/Gain Phase Analyzer (HP 4194 A). The heat filter was used to avoid the additional heating effects

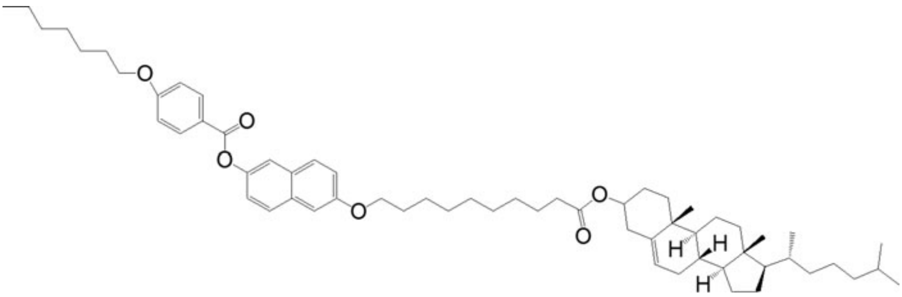

Figure 1. The molecular structure of chiral nematic liquid crystal (N*LC) 2-(cholesterol-n-decanoate)-6-(heptyloxy benzoate) naphthalene.

due to the UV irradiation during the experiment. The X-Ray diffraction spectra were recorded by X-Ray diffractometer (Model-Bruker D8 Advance X-ray diffractometer) for $0^{o} \leq 2\theta \leq 30^{o}$ using CuK$_{\alpha}$ radiation ($\lambda = 1.5418$ A°). The polarizing optical micrographs (optical textures) were recorded on the polarizing optical microscope (RXLr-5) under the crossed polarizer-analyzer condition.

Sample cell preparation

The LC sample cell with planar alignment was prepared using the two optically flat glass substrate coated with Indium Tin Oxide (ITO). The complete procedure of the sample cell fabrication has already been reported by our group [23]. The cell thickness was maintained ~ 10 μm by placing a Mylar spacer. The empty sample cell was calibrated using analytical reagent (AR) grade Carbon tetrachloride (CCl_4) and Benzene (C_6H_6). The N*LC was filled in the sample cell at a temperature higher than the isotropic temperature of N*LC sample by capillary method.

Dielectric loss measurement

The dielectric relaxations and dielectric loss were analyzed by the Cole-Cole relation. On separating the real and imaginary part of the Cole-Cole equation, the imaginary part gives the

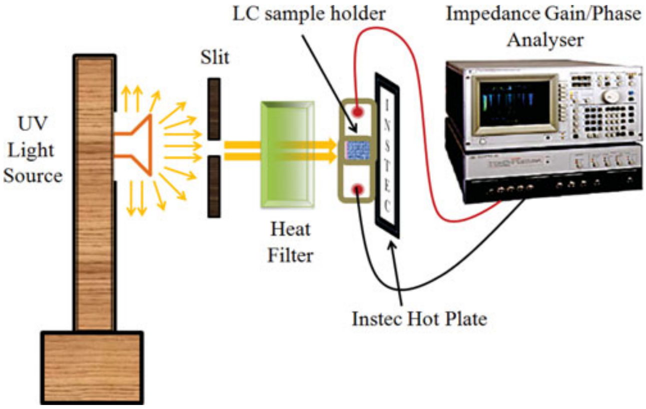

Figure 2. The experimental setup used in the present study to analyze the effect UV irradiation on N*LC.

value of dielectric loss. The detailed information about the calculation of the real and imaginary parts of the Cole-Cole relation has already been reported recently by Singh et al. [24].

Results and discussion

The N*LC, used in the present study is photo-responsive in nature due to the presence of cholesterol functional group. The geometrical shape of N*LC molecules is rod like. It is assumed that the rod like structure of N*LC molecules changes into the bend structure. During the UV irradiation process, N*LC absorb UV photonic energy which increases the total energy of the LC system. At this stage, LC system tries to minimize its surface area due to inertia. This process leads the bending of N*LC molecules after UV irradiation. The increase in pitch of chiral nematic LC by UV irradiation has already been reported by Yamaguchi et al. [25]. The similar result has also been observed in the present investigation. The increase in pitch of N*LC due to UV irradiation has been demonstrated by a suitable paradigm as shown in Fig. 3. The change in pitch was concluded by the reflected colour in the optical texture (POM image) of N*LC after UV irradiation. Pristine N*LC reflects blue colour in the optical texture whereas the UV irradiated N*LC reflects a combination of green and yellow colour which suggest the increase in pitch value of N*LC after the UV irradiation.

Figure 4 shows the X-Ray diffraction spectra of N*LC before and after UV irradiation at 146°C. Two diffuse peaks were observed nearly at 3° and 19° on 2θ scale. It is clear (Fig. 4) that the XRD spectra of UV irradiated N*LC is slightly different with that of the N*LC without UV irradiation suggesting the change in cholesteric plane-spacing (CPS). When N*LC is irradiated by the UV light, the cholesteric plane-spacing increases due to the absorbance of UV photonic energy. The increased cholesteric plane-spacing leads higher pitch value of the N*LC after UV irradiation. The cholesteric plane-spacing between the N*LC molecules, before and after the UV irradiation was found to be 7.71 and 8.12 nm, respectively. The similar observation describing the change in cholesteric plane-spacing has been reported in the literature [26].

The polarizing optical micrographs (optical textures) of N*LC before and after UV irradiation are shown in Fig. 5 which were taken at 146°C and between crossed polarisers. Figure 5a shows the optical texture of N*LC without UV irradiation whereas the optical textures presented in Fig. 5b and 5c were taken after the 10 minutes (10 mJ/cm^2) and 25 minutes

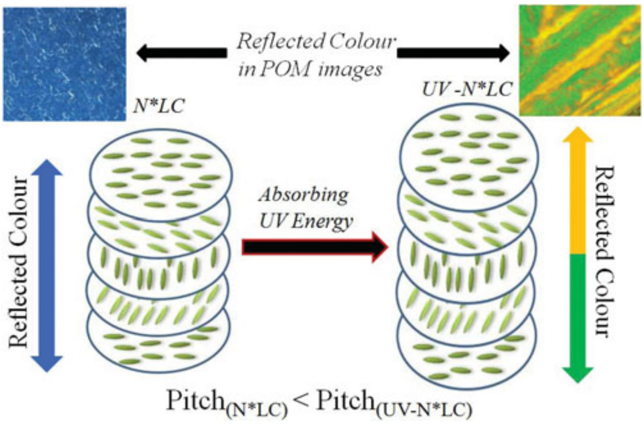

Figure 3. The probable paradigm of the change in pitch of the helical structure of the N*LC under UV irradiation and corresponding reflected colours observed in POM images.

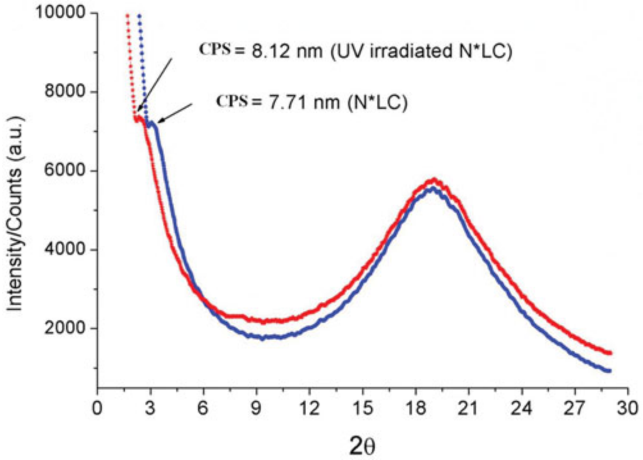

Figure 4. X-Ray diffraction spectra of the pure N*LC and UV irradiated N*LC.

(25 mJ/cm^2) exposure of UV radiation respectively. The higher dose of UV exposure was avoided due to uncontrolled alignment of LC molecules and enhanced mobility of the mobile ions in LC sample. Han et al. [27] has also reported the need of small UV doses for the better photo-alignment of LC molecules using linearly polarized UV irradiation. Figure 5d was taken at isothermal state of UV irradiated N*LC after the removal of UV exposure. As UV light is allowed to fall on N*LC, the N*LC molecules absorb the UV photonic energy and become more energetic, therefore, the ordering of N*LC reduces and cholesteric plane spacing of the molecules changes. Due to change in the ordering and cholesteric plane spacing, the value of pitch also changes. The change in pitch results a change in the reflection colour of N*LC under polarized light. As we increase the exposure time of UV irradiation (from 10 to 25 min.), the N*LC molecules become high energetic and behave like free dipoles. This stage (when high energetic molecules behave like free dipoles) introduces an isotropy in the LC medium. The state of isotropy (black regions) has been clearly observed in Fig. 5c. UV exposure dose was

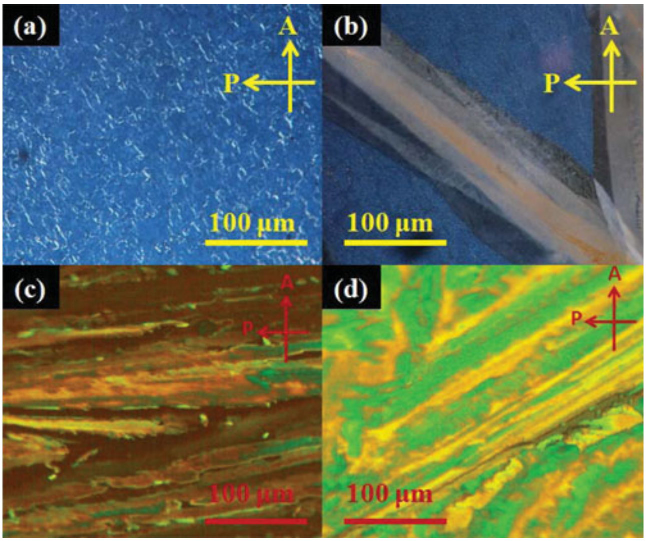

Figure 5. The polarizing optical micrographs at 146°C for (a) pure N*LC, (b) after 10 minutes during UV irradiation, (c) after 25 minutes during UV irradiation and (d) at isothermal state after UV irradiation.

not exceeded beyond this limit because of the occurrence of uncontrolled order to disorder transitions. As we remove the UV exposure, N*LC molecules achieve an isotheral state after some time. At this isothermal state, a planar optical texture of green and yellow colour was observed as shown in Fig. 5d. The change in reflection colour indicates the change in pitch of N*LC after UV irradiation. The new reflected colour associated with the chiral nematic phase after UV irradiation indicates the 'Red shift' in the reflected wavelength. Optical textures also support the red shift in the reflected colour of the N*LC molecules after UV irradiation. Due to UV irradiation, the change in geometrical shape, reflection colour and cholesteric plane spacing are irreversible in nature which indicates that the present N*LC sample has lesser elastic properties and can be utilized in fracture detection in the materials at high temperature. As UV light is exposed on the N*LC, the photonic energy is instantaneously absorbed by the molecules. Subsequently, the thermal relaxation process is not similar for all the constituents (cholesterol and naphthalene functional group) of N*LC compound therefore, they form various regions of different ordering as observed in optical textures.

The behavior of a.c. conductivity on the temperature sacle for N*LC before and after UV irradiation is depicted in Fig. 6. The a.c. conductivity was calculated at 100 Hz frequency. The a.c. conductivity of the irradiated and non-irradiated N*LC is almost temperature independent except at the vicinity of Cr-N* phase transition temperature. The conductivity of UV irradiated N*LC is approximately 200 folds with that of the non-irradiated N*LC. This enormous increment in the a.c. conductivity is associated with the huge release of charge carriers and their increased mobility. These charge carriers with enhanced mobility result the tremendous increase in conductivity of N*LC after UV irradiation. The UV irradiated N*LC reflects optical colour of lesser wavelength (a combination of green and yellow colour) as compared to the non-irradiated N*LC of blue colour. Thus, the absorbed UV photonic energy is stored in LC molecules and they radiate a lesser amount of energy. The reflected colour by the UV irradiated N*LC is of longer wavelength as compared to N*LC without UV irradiation which suggests the application of UV irradiated N*LC in high temperature optical energy storage.

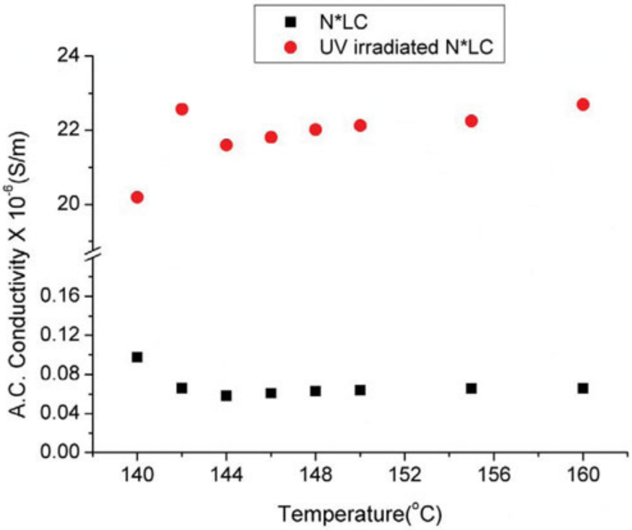

Figure 6. The behavior of a.c. conductivity on the temperature scale for the N*LC before and after UV irradiation.

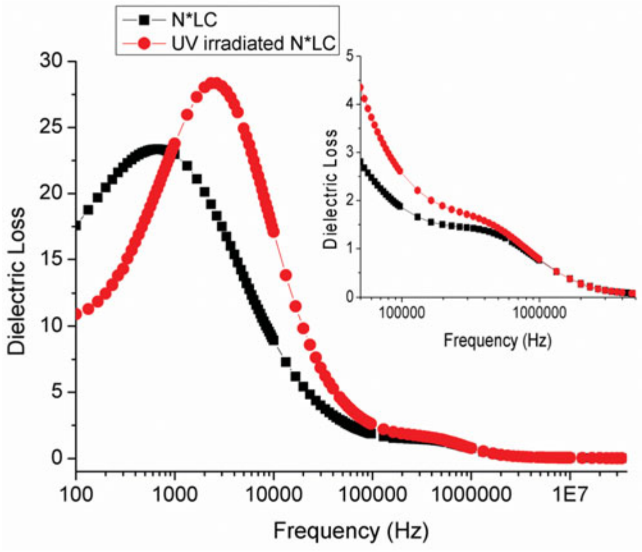

Figure 7. The variation of Dielectric Loss on the frequency scale at 144°C for N*LC and UV irradiated N*LC. The inset of Figure represents the enlarge portion of the dielectric loss from frequency 5 KHz to 5 MHz.

The absorption curves (dielectric loss vs. frequency) of N*LC before and after UV irradiation at 146°C are shown in Fig. 7.The inset (Fig. 7) represents the zoomed region of the absorption curve for the frequency interval of 5 KHz- 5 MHz. The N*LC without UV irradiation shows two relaxations near 1 KHz and 500 KHz which are associated with the rotation of molecules along the long and short molecular axis respectively. When N*LC is irradiated by UV light, the rod like molecules convert into bend shape molecules. In the bend structure, long molecular axis becomes shorter whereas short molecular axis remains unchanged. Therefore, the relaxation mode corresponding to the rotation of molecules along the long molecular axis shifts towards the higher frequency side and relaxation mode corresponding to rotation of molecules along the short molecular axis remains unaffected under the influence of UV irradiation.

Figure 8 shows the UV-visible absorbance of the N*LC before and after the irradiation. As the absorption of incident light depends upon the nature of surface (or shape) of material, therefore the drastic change in the absorbance of UV irradiated N*LC indicates the change in surface or shape. Zhao et al. [28] has already reported the change in absorption spectra of liquid crystalline azobenzene-containing diblock copolymers due to the polarized UV irradiation. Every surface including molecular surfaces has surface tension. As we irradiate the N*LC molecules by UV light, the energy of the molecules increases. At this stage, the molecules try to minimize their surface area due to surface tension. Under this physical law, rod like N*LC molecules adopt a degree of bending. This bending in the shape of N*LC molecules after UV irradiation produces the modification in the physical properties.

The cholesteric plane spacing, bending energy, relaxation strength, and distribution parameter have also been calculated for the N*LC before and after UV irradiation. The change in above mentioned physical parameters has been listed in Table 1.

The cholesteric plane spacing between the N*LC molecules has been increased due to the UV irradiation. The cholesteric plane spacing of the N*LC molecules was increased from 7.71 to 8.12 nm after UV irradiation. This increase in the cholesteric plane spacing is analogous to increase in the pitch value, therefore the reflected colour in the optical texture also changes.

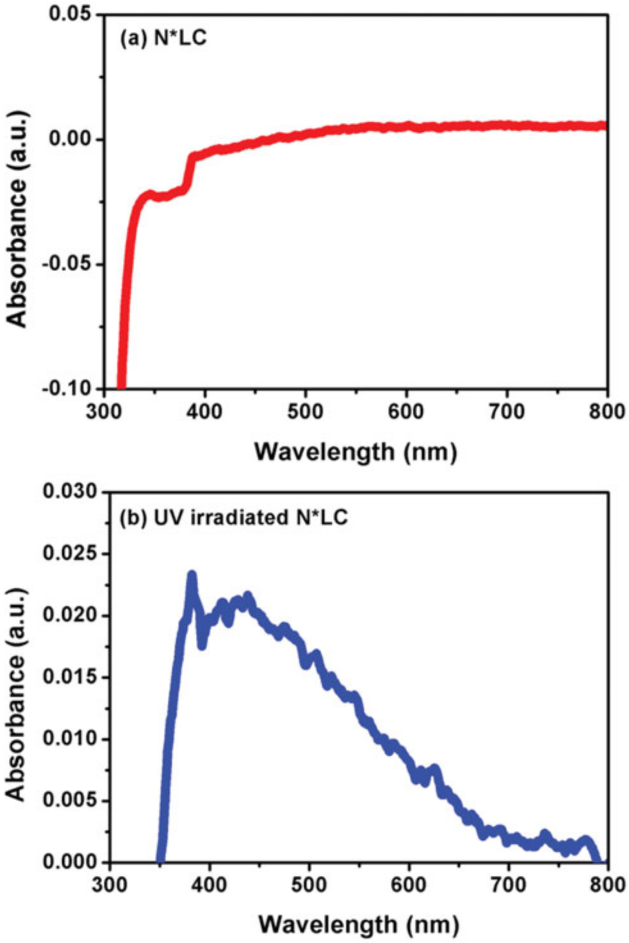

Figure 8. The UV-visible absorption spectra of N*LC before and after UV irradiation. The UV-Visible measurements were made in solution taking the ethanol as solvent.

Similarly, the bending energy of N*LC before and after UV irradiation was found to be 28.34 and 47.17 Kcal/mol, respectively. The relaxation strength and distribution parameter of N*LC have also been altered due to the UV irradiation. The value of relaxation strength for N*LC reduces approximately 1.8 fold as compared to nonirradiated N*LC. The distribution parameter also decreases approximately 2.2 fold after irradiating the N*LC by UV light. The change in relaxation strength and distribution parameter for the UV irradiated N*LC shows agreement with the shifting of relaxation mode due to the rotation of modified long molecular axis and sharpness of relaxation mode, respectively [24].

Table 1. Various physical parameters of N*LC with and without UV irradiation.

Parameters	$d_{spacing}$ (nm)	Bending energy (Kcal/mol)	Relaxation strength ($\Delta\varepsilon$)	Distribution parameter (α)
N*LC	7.71	28.34	65.47	0.123
UV irradiated N*LC	8.12	47.17	36.40	0.054

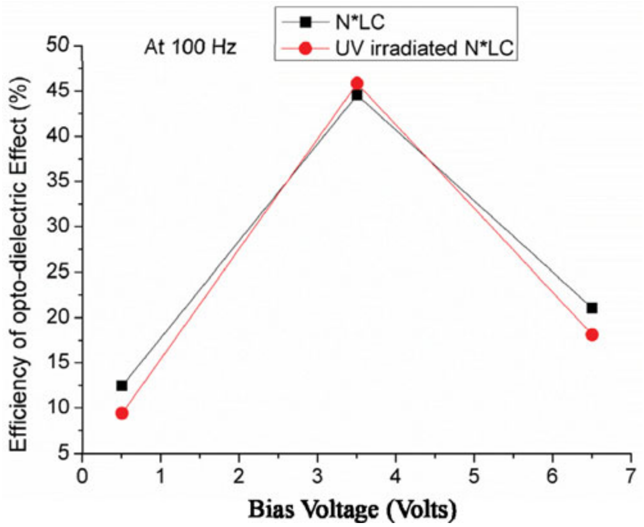

Figure 9. The efficiency of opto-dielectric effect on the bias voltage scale calculated at 100 Hz for the N*LC before and after UV irradiation.

The efficiency of opto-dielectric effect [13] with the variation of bias voltage was estimated by using the relation

$$\eta_{\mathrm{ODE}} = \frac{\varepsilon_{\perp \mathrm{UV}} - \varepsilon_{\perp \mathrm{NoUV}}}{\varepsilon_{\perp \mathrm{NoUV}}} \times 100 \tag{1}$$

The variation of efficiency of opto-dielectric effect with the change in bias voltage has been plotted in Fig. 9. The efficiency of opto-dielectric effect is maximum at 3.5 V which indicate the value of threshold operating potential of N*LC sample. The maximum efficiency of opto-dielectric effect (at 3.5 V) is almost independent of UV irradiation.

Conclusions

In summary, we analyzed the photo-irradiation effects on the chiral nematic (N*) phase of a LC material. The controlled exposure of UV light on the N*LC alters its physical properties. Absorbing the UV photonic energy, the rod like N*LC molecules adopt a degree of bending. The exposure of UV light also changes the cholesteric plane spacing of N*LC molecules which results a change in the pitch value. Due to change in pitch, the reflected colour in the optical texture has also been changed. Without UV irradiation, the N*LC reflects blue colour whereas after UV irradiation, it reflects the combination of green and yellow colour. This result indicates a red shift in the reflected colour by the N*LC after irradiated with UV light. The a.c. conductivity of N*LC increases enormously due to the absorbance of UV photonic energy. The change in shape of N*LC molecule due to the UV irradiation affect the long molecular axis and thus the relaxation mode due to the rotation of molecules along the long molecular axis shifts towards higher frequency side. The maximum efficiency of the opto-dielectric effect was observed at 3.5 V bias voltage which indicates the use of present system in high temperature photonic application instead of its use in display. At present, UV irradiation is widely used for the alignment of the LC molecules. The change in geometrical shape, reflection colour and cholesteric plane spacing due to UV irradiation are irreversible in nature which indicates that the present N*LC sample has lesser elastic properties and can be utilized in fracture detection at high temperature. The present study suggests that the UV irradiation may also be a useful tool to tune the properties of a materials and its application in optical energy storage devices at high temperature.

Acknowledgments

The authors are thankful to Department of Science and Technology, Government of India for the financial assistance for present work in the form of project. The authors DPS and SKG are thankful to CSIR, India For the grant of SRF fellowship Nos. 09/107(0363)/2012-EMR-I and 09/107(0337)/2010-EMR-I respectively. DPS is also thankful to CEFIPRA for Raman-Charpak fellowship in France. TV is thankful to UGC for BSR fellowship. RM is thankful to UGC for research award.

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