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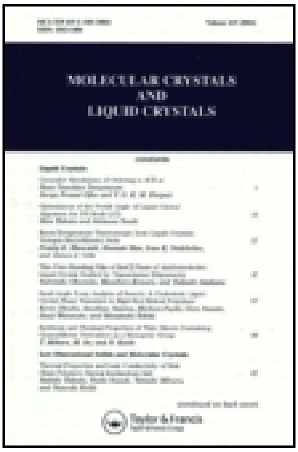

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Thermal Characterization of Induced Mesomorphism in Binary Mixture of Cholesteryl and Poly Ethylene Glycol

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We report the results of our studies on optical and thermal properties of two compounds viz., cholesteryl linolenate and poly ethylene glycol exhibits very interesting liquid crystalline-induced lamellar smectic phases at large range of concentrations and temperature. The mixture with lower and higher concentrations of poly ethylene glycol (PEG) exhibits an Iso-N-SmA-SmE-Cry, sequentially when the specimen is cooled from its isotropic phase. But concentrations from 20% to 40% of the mixture exhibit a SmC* phase. Different phases were observed in the mixture and are identified using X-ray and microscopic techniques. The temperature variation of optical anisotropy and helical pitch measurements are also discussed.*

Keywords Binary mixture; mesomorphic phases; non-mesogenic

Introduction

The cholesteric phase (N*) is regarded as twisted nematic wherein the molecules are orientiationally ordered, but at the same time they are rotationally disordered with respect to long axis [1–6]. It is well known that, if small percentage of cholesteric liquid crystal is added to nematic, it results in the helical distortion and pitch of the phase is increased. When the pitch is comparable to the wavelength of light, the phase becomes iridescent because of the selective reflection of light. The mixture of cholesteric and nematic liquid crystals reveals that, the mixture exhibits frustrated blue phase, twisted grain boundary phase, tilted phase, cholesteric phase(N*), and quasicrystalline phase [7–9], because of the tremendous potentialities of the liquid crystals in the field of display device technology.

Here, we have proposed the studies on thermal and optical properties of the binary mixture of cholesteryl and PEG. The optical, thermal and X-ray studies have been carried out to understand the intermolecular interactions and nature of the induced lamellar smectic phases exhibited by the mixture.

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Experimental Studies

In the present investigation, we have considered the binary mixture of two compounds viz., cholesteryl linolenate and PEG. Cholesteryl Linolenate was obtained from M/s Eastmann Organic Chemicals USA. The PEG was supplied by M/S SISCO Research Laboratory, Bombay, India. Mixtures of 20 different concentrations of PEG in cholesteryl linolenate were prepared, the phase transition temperatures of the mixture were determined using Leitz-polarizing microscope in conjunction with hot stage. Differential scanning calorimeter (DSC) thermograms were taken for all concentrations of the given mixture using Perkin-Elmer DSC II Instrument facility available at Raman Research Institute, Bangalore, India. The values of phase transition temperatures of the mixture were found to be in good agreement with the values obtained from DSC and optical texture studies. The density and refractive indices of the mixtures were measured at different temperatures employing the technique described in our earlier paper [10]. The X-ray diffraction studies were undertaken by using JEOL X-ray diffractometer at various temperatures for different concentrations of the mixture.

Results and Discussions

Phase Diagram

The binary mixture of PEG and cholesteryl linolenate exhibits a different liquid crystalline phases, the phase transition temperatures were measured by using Leitz-polarizing microscopic. The partial phase diagram shown in Fig. 1, which is obtained by plotting the concentrations against the phase transition temperatures of the mixture, which clearly illustrates that, the mixture of lower and higher concentrations of PEG and cholesteryl linolenate exhibit a cholesteric phase (N*) and also an induced smectic phases like SmA, SmC*, and SmE phases, but at the middle of the concentrations we have been observed only chiral SmC* phase along with the above mentioned mesophases, respectively, when

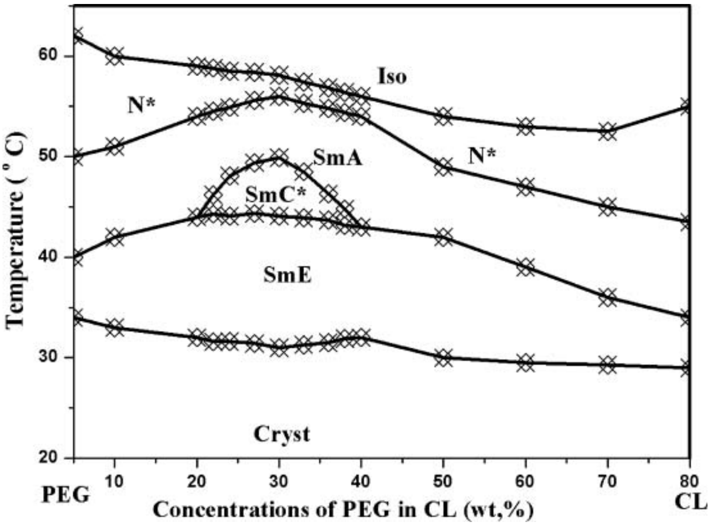

Figure 1. Partial phase diagram for the mixture of PEG and CL.

the specimen is cooled from its isotropic liquid phase. The concentrations from 20% to 40% of the mixtures exhibit cholesteric (N*), SmA, SmC*, and SmE phases.

Optical Texture Studies

For the purpose of optical texture studies, the sample was sandwiched between the slide and cover glass and then the optical textures were observed using Leitz-polarizing microscope in conjunction with specially constructed hot stage. The concentrations ranges from 5% to 80% of the mixture are slowly cooled from its isotropic melt, the genesis of nucleation starts in the form of small bubbles and slowly grow radially, which form a spherulitic texture of cholesteric (N*) phase with large values of pitch is shown in Fig. 2(a) [11,12]. On further cooling the specimen, the cholesteric (N*) phase slowly changes over to focal conic fan shaped texture, which is the characteristics of SmA phase as shown in Fig. 2(b). The concentrations from 20% to 40% of the mixture, the SmA phase changes over to SmC* phase, which exhibit a radial fringes on the fans of focal conic textures, which are the characteristics of chiral Smc* phase as shown in Fig. 2(c). On further cooling the specimen, Smc* phase changes over to SmE phase, which remains up to room temperature and then it becomes a crystalline phase.

Optical Anisotropy

Results of this investigation are further supported by the optical studies. The refractive indices for extraordinary ray (n_e) and ordinary ray (n_o) of the mixture were measured at different temperatures for the different concentrations using Abbe Refractometer and Precission Goniometer Spectrometer. The temperature variations of refractive indices for 30% of PEG in cholesteryl linolenate are shown in Fig. 3. The values of electrical susceptibility for 30% of PEG in cholesteryl linolenate have been calculated using Neugebauer relation [13] at different temperatures. The temperature variations of electrical susceptibility for the mixture are as shown in Fig. 4. From this figure, it can be observed that wherever there is a phase transition, the value of electrical susceptibility changes appreciably, which indicates

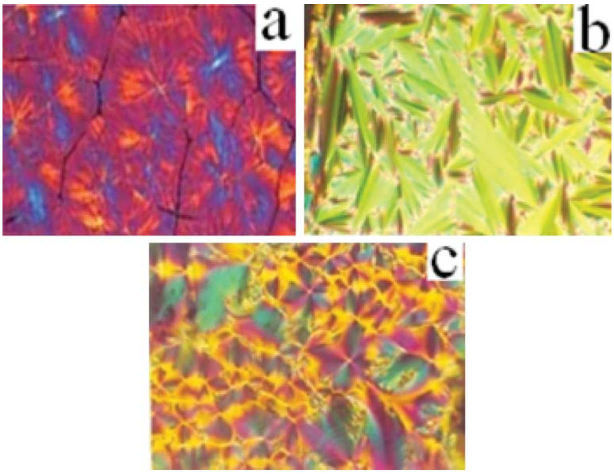

Figure 2. Microphotographs showing, (a) cholesteric phase (180×). (b) Focal conic fan-shaped texture of Smectic-A phase (180×). (c) Chiral Smectic-C* phase (180×).

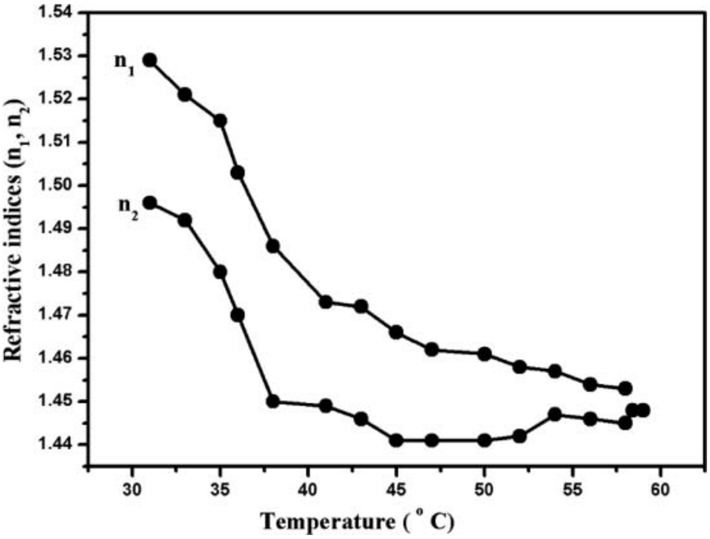

Figure 3. Temperature variations of refractive indices for the mixture of 30% PEG in CL.

that each change corresponds to induced mesomorphic phases. Further with increasing the temperature of given concentration of PEG, the value of electrical susceptibility decreases, because the effective optical anisotropy associated with the molecules of poly ethylene glycol also decreases. But here in this graph, we have observed an auxiliary peak in addition to the main peak, which illustrates that, the peak cannot be thought only due to change in the orientation of molecules. They can be attributed to changes in the dimension of molecules along with changes in orientation.

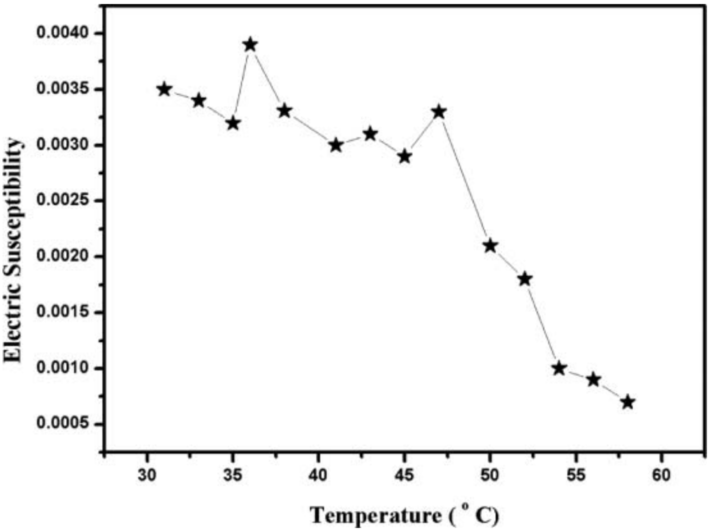

Figure 4. Temperature variation of electrical susceptibility for the mixture of 30% PEG in CL.

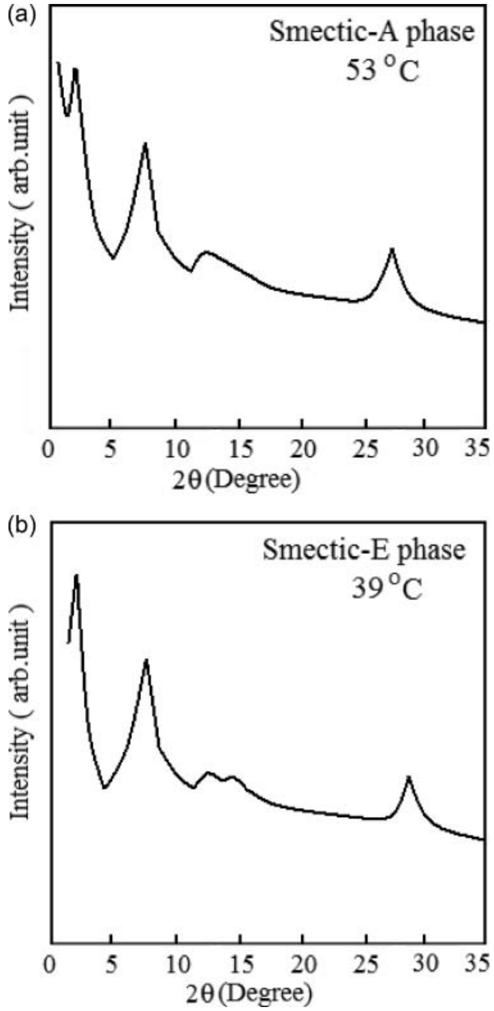

Figure 5. (a) XRD traces obtained for the mixture of 30% of PEG in CL at 53°C in Smectic-A phase. (b) XRD traces obtained for the mixture of 30% of PEG in CL at 39°C in Smectic-E phase.

X-Ray Studies

Using XRD data, an attempt has been made to understand the molecular arrangement in the mixture of PEG in cholesteryl linolenate. The X-ray diffraction patterns were recorded using JEOL (Japan), X-ray diffractometer (target Fe $\lambda = 1.934$ Å). The X-ray diffractometer traces were obtained for 30% of the mixture at temperatures 39°C and 53°C, respectively, in SmA and SmE phases as shown in Figs. 5(a) and (b). Here, it is observed that the peaks are very sharp in the SmE phase [14], because of the fact that the SmE phase is highly ordered. The effective "*d*" spacings in SmE phase are calculated using the Bragg's equation are shown in Table 1. The sharp peak in the X-ray recordings correspond to the first-order diffraction from the smectic layer like planes, from which *d* is calculated. The intermolecular distance is calculated from the broad peak, which appears to be sharp owing to the fact that within the plane of each layer there is a regular arrangement of molecule in the lateral directions.

Table 1. Spacings determined using XRD recordings, calculated values of *S*, the interfacial area per polar group, and d_{hc}, the average thickness of the hydrocarbon layers obtained for different concentrations of PEG in CL

	S_{mE} phase					S (10^{-2} nm^2)	
PEG content (wt%)	d (10^{-1} m)	Volume fraction (φ)	D (10^{-1} nm)	d_{hc} (10^{-1} nm)	d_{eg} (10^{-1} nm)	S_{mE} phase	S_{mA} phase
10	32.35 (15.69)	0.8615	4.12	28.15	4.5796	23.87	—
20	34.16 (15.74)	0.8645	4.69	29.65	4.6984	22.85	49.56
30	36.86 (13.75)	0.8605	4.89	31.59	5.2102	21.06	45.39
40	41.56 (13.23)	0.8615	4.55	36.03	5.7971	19.62	42.67
50	50.28 (13.84)	0.8609	4.67	43.45	5.1389	15.69	35.89
60	37.13 (15.79)	0.8625	4.17	31.69	5.1992	21.85	—

In light of the above-mentioned arguments, it is clear that, the nonaqueous binary mixture of PEG and cholesteryl linolenate exhibits an induced smectic phases at all temperature. The experimental X-ray recordings confirm that these mesophases are an induced lamellar smectic phases. The molecular length of PEG is 2.19 nm, which is calculated from the skeletal structure of PEG using the bond lengths. The effective "*d*" spacings were obtained from X-ray recordings at temperature 39°C approximately corresponds to twice the molecular length of PEG.

The area per polar group (*S*) in different lamellar phases was calculated using the standard method [15]. Hence, we observe that the molecular area of polar head at high temperature is equal to twice the molecular area of the crystallized aliphatic chains at lower temperatures [16]. Figure 6 shows a planar bimolecular leaflets alternating with ethylene glycol regions in one-dimensional liquid crystalline lattice. hc designates the pure polyethylene glycol region and circles denotes the interface between the hydrocarbons and

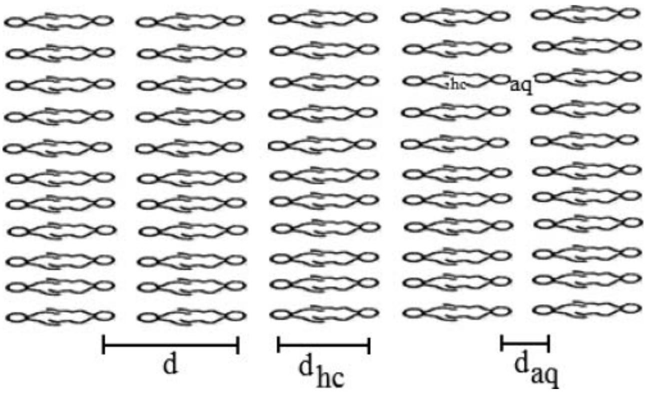

Figure 6. Planar bimolecular leaflets alternating with polyethylene glycol regions in one dimensional liquid crystal lattice.

ethylene glycol. The interfacial area per molecule (*S*) is calculated and these values are shown in Table 1.

Helical Pitch (Smectic and Cholesteryl Layers) Measurements

The helical pitch measurements were performed on the cholesteric (N*) phase following the well-known Grandjean–Cano wedge method [17,18]. The binary mixture was taken in a wedge-shaped cell treated for homogeneous alignment. The two glass plates formed a small angle at the wedge. The mixture was cooled slowly (0.2°C min^{-1}) from isotropic cholesteric (N*) phase to smectic phase, which induces an array of equidistant Grandjean–Cano lines. The pitch of the cholesteric (N*) phase was determined by measuring the distance between the Grandjean–Cano lines as a function of temperature. As the temperature was lowered from the cholesteric (N*) phase to smectic phase, spacing between the lines are increased, indicating that the pitch in the cholesteric (N*) phase are also increasing. The temperature variation of pitch for the mixture of 30% PEG in cholesteryl linolenate is shown in Fig. 7. From this figure, it is evident that, the variation of pitch from cholesteric (N*) to smectic phase is smooth and continuous. But gradually, the value of pitch increases from 0.17 to 0.19 mm was observed upon cooling the sample from cholesteric (N*) phase to smectic phase. The value of the pitch increased steeply and reached a maximum of 0.55 mm at the cholesteric (N*) to smectic phase transition.

But in the studies, we have noticed that, the sequence is Iso-N*-SmA-SmC*-SmE phases on cooling. Most of the data about the helical pitch have been given previously in Ref. [19]. The pitch is continuous at the N*-smectic transition in spite of a rather energetic transition. It increases on cooling to smectic phase and diverges on approaching the SmA and SmC* phases. This divergence related to the second-order nature of the transition. It exhibits a steep decrease, close to cholesteric (N*) phase which is usually the characteristics of second-order SmA, SmC* phase transitions.

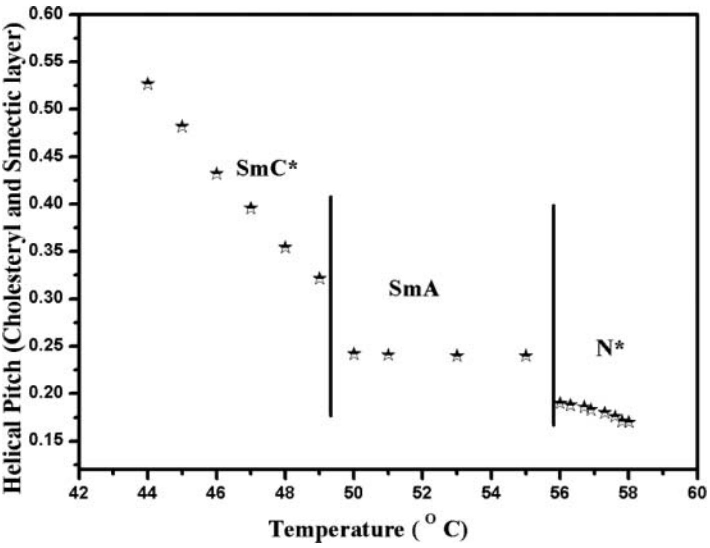

Figure 7. The temperature variation of helical pitch for the mixture of 30% PEG in CL.

Conclusions

The above studies apart from revealing a numerous textures and are associated with the various phases in the mixture have been enabled us to reach the following conclusions. The mixture with different concentrations from 5% to 80% of PEG in cholesteryl linolenate exhibit induced lamellar smectic phases depending on the temperatures. The drastic change in the value of density, refractive index, optical anisotropy of polarizabilities with the temperature unambiguously corresponds to SmA and SmE phases. The X-ray results also lend support to the above observations. The concentration ranges from 5% to 80% of the mixture exhibit a cholesteric (N*) phase. Here, the pitch is continuously increasing at the transition from cholesteric (N*) to smectic phase transition. But, it is very interesting to increases on cooling to smectic phase, which evidently diverges on approaching the SmA and SmC* phases, respectively.

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