

Phase Morphology in Liquid Crystals Mixtures

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Abstract: Investigations on the phases of Cholesteryl and nematic binary mixtures with varying concentrations were carried out using Fabry Perot Scattering Studies (FPSS), Differential Scanning Calorimetry (DSC), and Polarizing Microscopy Studies (PMS). Structural analyses were performed by the Fourier Transform Infra Red (FTIR), spectroscopy, absorptions spectra from Ultraviolet – Visible (UV) and Refractive Index (RI). The concentration of the cholesteric and nematic compound proved to have significant effect on the phase transitions, resulting in the appearance of new mesophases. The new transition temperature obtained from FPSS measurements agree well with the PMS and DSC.

Keywords: Liquid Crystals (LC), Polarizing Microscopy Studies (PMS), Fourier Transform Infra Red (FTIR), Differential Scanning Calorimetry (DSC), Ultraviolet (UV) Spectroscopy, Refractive Index (RI).

1. Introduction

Liquid Crystals (LC) are materials that are structurally intermediate between solids and liquids, which make them unique model. Many liquid crystal sub-phases are defined by the degree of positional and orientational ordering of the molecules and the materials that make up these liquid crystal phases. One is thermotropic liquid crystals, which exhibit mesomorphic behaviour within certain temperature range. The mesophase of thermotropic liquid crystals are thermodynamically stable, but only partially ordered phase. Each mesophase is described by its degree of order. LC materials generally have several common characteristics; one of the characteristics is the phase transition temperature which is measured over temperature range. To achieve useful temperature range, various mixtures can be used. The miscibility of the low molar LC is important both for the identification of various liquid crystalline phases and for the preparation of mixtures with well defined phase transitions. Arnold, Scakmann and Demus developed the miscibility rules [1 – 3] which can be summarized: 1) If two LCs are miscible, they are isomorphic and therefore belong to the same type of mesophase. 2) If two LCs are isomorphic, they need not necessarily be miscible. When two compounds are isomorphic within a certain mesophase, both their thermal transition temperatures and corresponding thermodynamic parameters exhibit continuous dependence on their composition, this means that both the components of mixtures behave like an ideal solution [4 – 8]. There are several methods used for characterization of various liquid crystalline phases Viz. Polarizing Microscopy Studies (PMS), Fabry - Perot Scattering Studies (FPSS), Fourier Transform Infrared (FTIR) Spectroscopy, Differential Scanning Calorimetry (DSC)/ Data Thermal Analysis (DTA) etc. We studied optical properties of 4 – cynophenyl-4n hexyl benzoate (Solid → Nematic → Isotropic) and cholesteryl pelargonate (Smectic → Cholesteric → Isotropic). The study of phase transition of thermotropic liquid crystal is done by FPSS.

The phase transition of liquid crystal between various mesomorphic forms occurs at a thermodynamically defined

temperature as the liquid crystal undergoes a change in internal order at the point of phase transition. 4 – Cynophenyl – 4n – hexyl benzoate exhibit mesophases of nematic phases. We used the FTIR technique for investigation of new functional group. PMS is used for texture study and comparison of transition temperature. In addition to this, we also observe Refractive index of entire sample.

2. Material and Methods

In this paper we used two sample (1) CLCs Cholesteryl pelargonate (97%) (A) and (2) 4-Cynophenyl-4n hexyl benzoate (97%) (B) and their mixtures in appropriate proportions by weight. We analyzed the transition temperatures using FPSS whereas we observe the textures and analyzed the transition temperatures as well as nature exhibited by liquid crystal phases using PMS. The Phase Transition temperature shows more complex behavior at the lower heating cycle and diverse concentrations. We observed, some interesting phases like, Structural changes due to various concentrations at various excitations were studied by FTIR. We found the different functional groups which are present in a molecule like all over the mixtures.

3. Observation

In FPSS studies, the angular diameters of the rings were measured at various temperatures. The temperatures were measured accurately using a Remote Sensing Infra-red Thermometer having a resolution of 0.1°C. Some new mesophase transition temperatures of the liquid crystals were also observed. As per FPSS, we are able to register some new PTTs in LCs. The different mesophase transition temperatures of the liquid crystals have been studied by using the simple spectroscopic technique. Diameter is decreases as the intensity of laser increases, but at the intensity with the dispersed polymer diameter increases. Temperature variation at various concentration of mixture of Pelargonate (A) + 4-n cynopheyl-4n-hexylbenzoate (B). The graph shows (Fig 1) variation of the angular diameter of rings Vs temperature. Each graph shows abrupt variation at

the mesophase transition temperatures of each of the liquid crystal samples investigated.

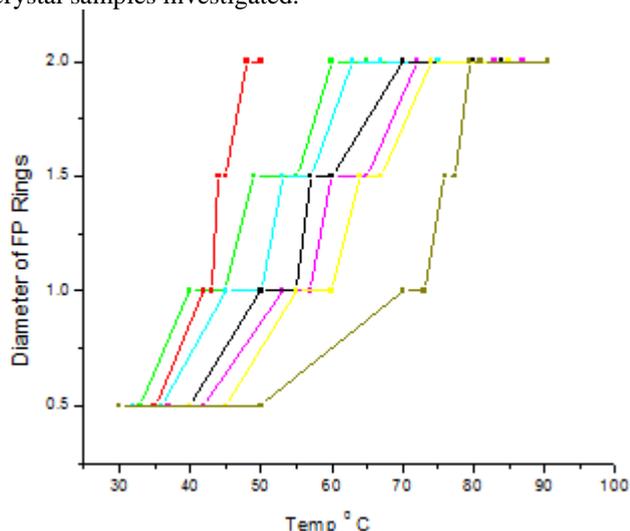


Figure 1: FPSS Observation of all composite liquid crystals.

In FPSS studies we found the mesophase transition temperature which has been confirmed by the other techniques such as Polarisation Microscopy Studies,

Differential Scanning Calorimeter/Data Thermal Analysis. Some new mesophase transition temperatures were obtained for the mixtures by this technique. PMS used to study textures of all LCs and their mixtures at different concentration. The textures were observed for both heating and cooling cycles of all samples. The nature of textures changes with change in concentration of cholesteric and nematic liquid crystals.

The textures are shown in fig. 2.



Figure 2.1: A-Focal conical (60°C)

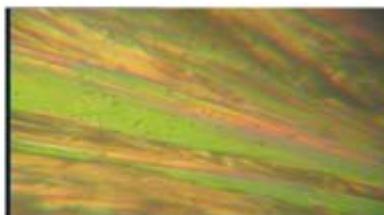


Figure 2.2: B- S_E with spherulitic region.(50°C)



Figure 2.3: A+B-Cholesteric oil streak (66°C)

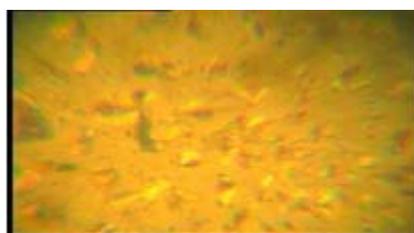


Figure 2.4: 2A+3B-Broken Fan (48°C)

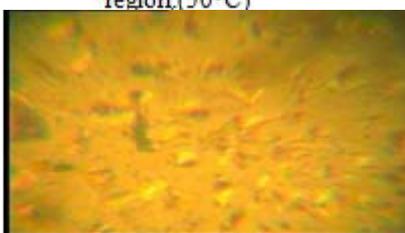


Figure 2.5: 3A+2B-Broken Fan (53°C)

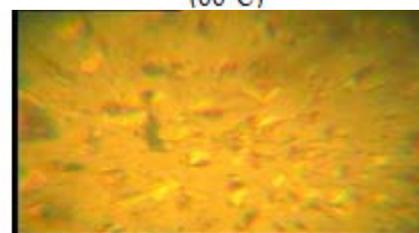


Figure 2.6: 3A+7B- Broken Fan (57°C)

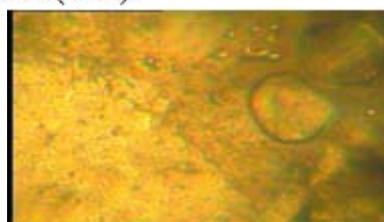


Figure 2.7: 7A+3B- Formulation fan texture (67°C)

The mesomorphic behavior of compound A and B was evaluated with the help of PMS and DSC/DTA. Cholesteryl Plargonate when heated exhibiting the textural pattern appeared at 55°C. On cooling, the mesophase appeared at 60°C exhibiting focal conic texture which remains unaltered till closed to room temperature. Nematic-cynophenyl-4n hexyl benzoate when heated it exhibiting the textural pattern marble like at 44°C, S_E with spherulitic region at 50°C, Due to various concentration of mixture of A and B texture like Cholesteric oil streak (66°C) at A+B, Broken Fan (48°C) at

2A+3B, Broken Fan (53°C) at 3A+2B, Broken Fan (57°C) at 3A+7B, Formulation fan texture (67°C) at 7A+3B. All these textures are vary from smectic to nematic are due to change in concentration. The liquid crystal samples were investigated using a Differential Scanning Calorimetry (DSC) or Data thermal analysis (DTA). It is a useful tool to study of liquid crystal phase transitions. Its utilization in determining the heat supplied or extracted during a process such as a phase transition is discussed in Thermal Properties of material. From DSC /DTA mesophase transition

temperature has been confirmed. The DSC of all composite liquid crystals at various concentrations are shown in fig.3

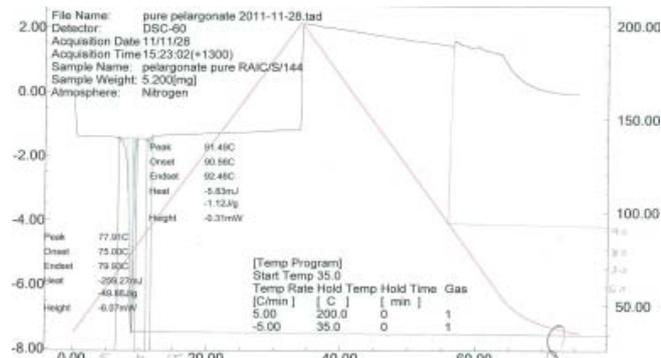


Figure 3.1: DSC of pure A

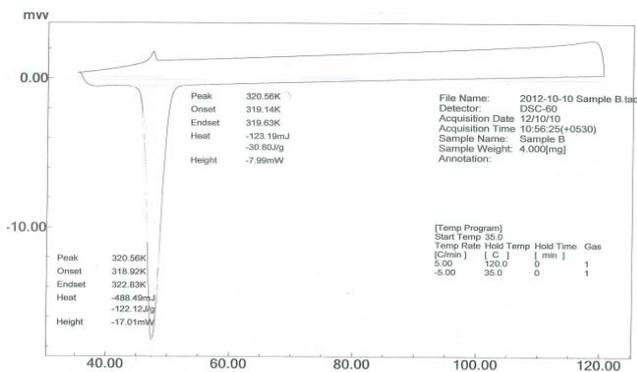


Figure 3.2: DSC of pure B

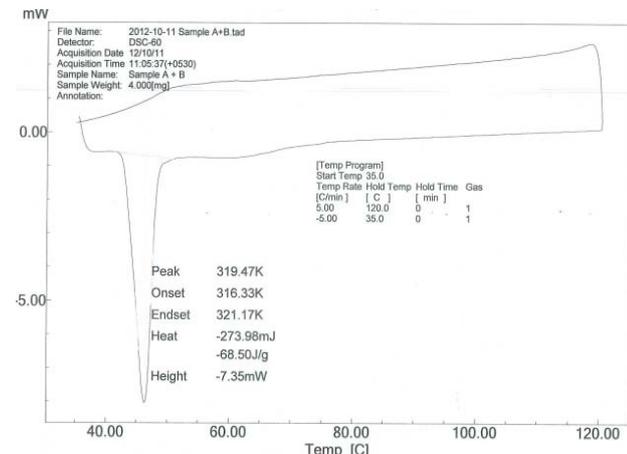


Figure 3.3: DSC of A+B

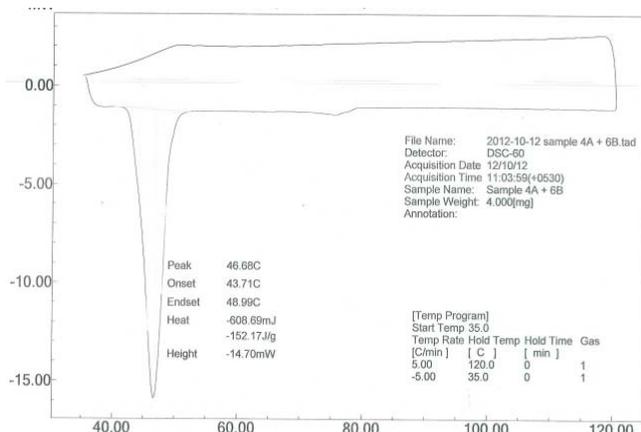


Figure 3.4 DSC of 2A+3B

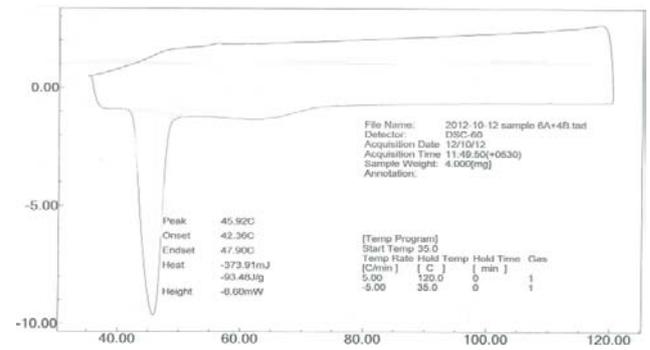


Figure 3.5: DSC of 3A+2B

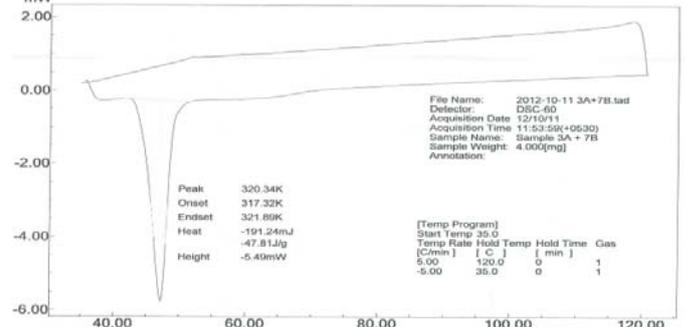


Figure 3.6 DSC of 3A+7B

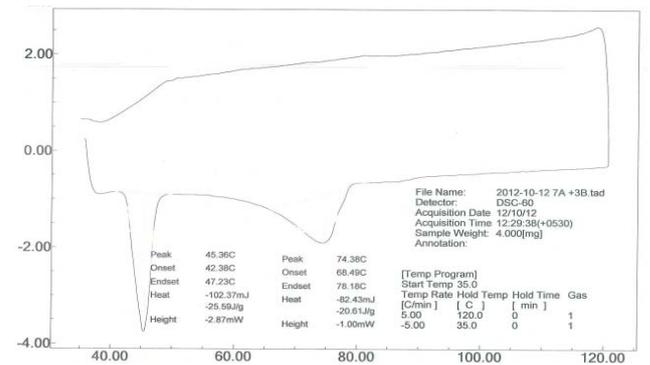


Figure 3.7: DSC of 7A+3B

The IR spectrum of a sample is recorded by passing a monochromatic beam of infrared light through the sample. From this, a transmittance or absorbance spectrum can be produced, showing at which IR wavelengths the sample absorbs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample. When the frequency of the IR is the same as the vibrational frequency of a bond, absorption occurs. Structural changes due to various concentrations at various excitations were studied by FTIR. In equal proportion of sample A and B we get highest peak intensity. There is no change of intensity when proportion in mixture is change from 3A+7B to 7A+3B. Whereas in case of mixture of 3A+2B intensity is more than mixture of 2A+ 3B. FTIR spectrographs were taken in the absorption as well as transmission mode and interpreted. The graph produced percentage transmission against wave number. Functional group observed in this analysis that was common for all concentration but some of peak or area of peak found with different functional or structural group. Aliphatic and carboxyl group are found. The FTIR of all composite liquid crystals at various concentrations are shown in Fig.3

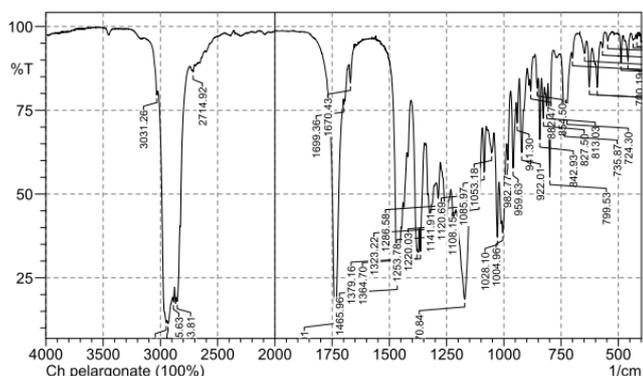


Figure 4.1: FTIR of Pure A

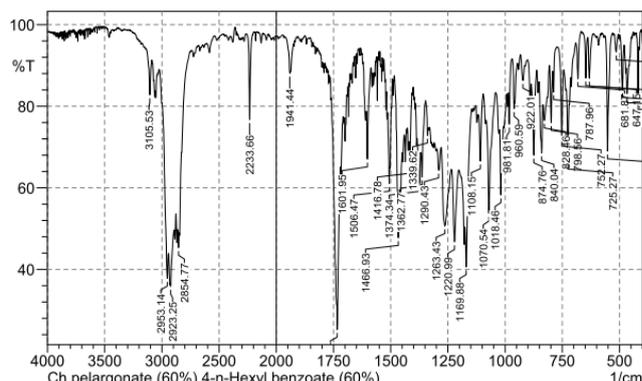


Figure 4.5: FTIR of 3A+2B

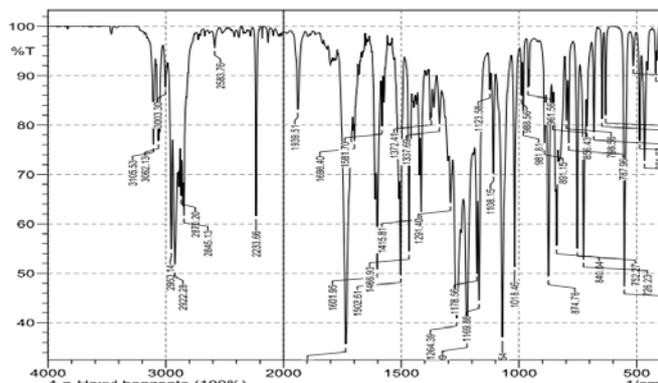


Figure 4.2: FTIR of Pure B

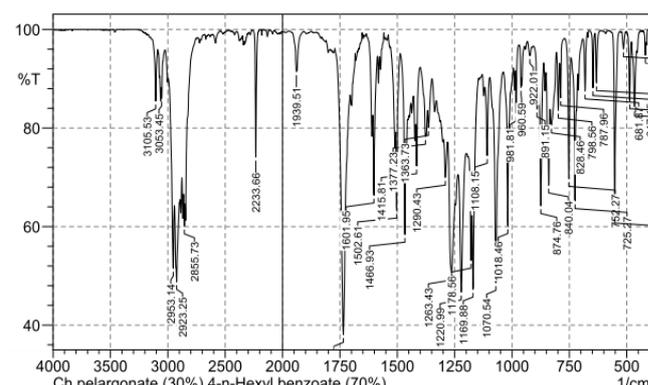


Figure 4.6: FTIR of 3A+7B

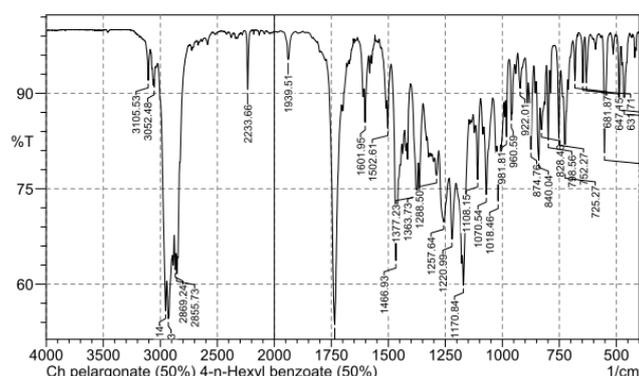


Figure 4.3: FTIR of A+B

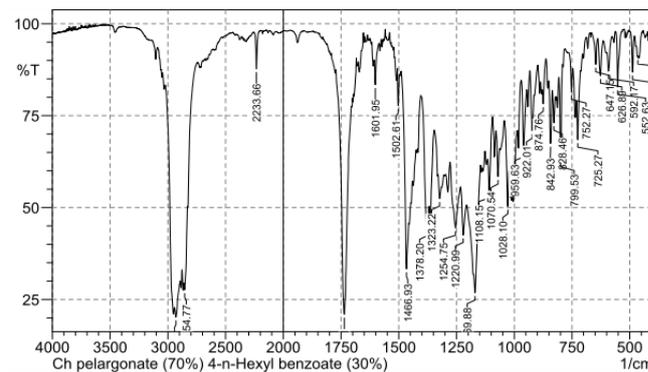


Figure 4.7: FTIR of 7A+3B

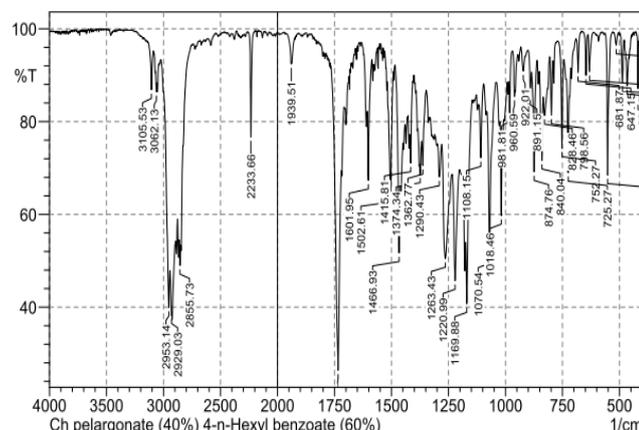


Figure 4.4: FTIR of 2A+3B

The peaks and corresponding bonds for composite liquid crystal and their mixtures is shown in Table 1:

Sample	Peak	Wavelength Range	Bond
A(100%)	735.87	600-900	O-H
	1004.966	1000-1100	oh
B(100%)	1178.56	1050-1300	C-O Alcohol
	1415.81	1340-1470	C-H Alkanes
	1601.95	1600-1700	C=O Aldehyde
5A(50%)+5B(50%)	647.15	600-700	C=CH
	681.87	690-900	O-H Phenols
	1377.23	4340-1470	C-H Alkanes
	1601.95	1600-1700	C=O Aldehydes
3A(30%) +7B (70%)	3103.53	3100-3200	Ammonium, Amide
	1457.55	1340-1470	C-HAlkanes.
	1733.43	1690-1760	R-C=O,Carboxylic Acid, C=O Aldehydes.
	2232.62	2210-2280	C=N Nitriles

	2958.25	2850-2970	C-H alkanes.
	3431.11	3200-3600	O-H Alcohol, Phenol
2A(40%) +3B (60%)	1724.97	1690-1760	R-C=O, Carboxylic Acid, C=O, Aldehydes.
	2231.95	2210-2280	C=N Nitriles
	2959.86	2850-2970	C-H alkanes.
	3430	3200-3600	O-H Alcohol, Phenol
3A(60%) +2B (40%)	1639.06,1731.87	1690-1760	R-C=O Carboxylic Acid, C=O, Aldehydes.
	2232.56	2210-2280	C=N Nitriles
	2955.52,	2850-2970	C-H alkanes.
	3431.44	3200-3600	O-H Alcohol, Phenol
7A(70%) +3B (30%)	1550.51	1500-1570	NO ₂ Nitro Compound.
	1722.51	1690-1760	R-C=O, Carboxylic Acid, C=O Aldehydes.
	2230.77	2210-2280	C=N Nitriles
	2957.97	2850-2970	C-H alkanes.
	3105.53	3200-3600	O-H Alcohol, Phenol

The peaks and corresponding bonds for composite liquid crystal and their mixtures is shown in Table 2:

A UV-Vis spectrophotometer measures the amount of light absorbed at each wavelength of the UV and visible regions of the electromagnetic spectrum. A UV or visible spectrophotometer has the same basic design as an infrared spectrophotometer. The UV analysis give peaks of all composite liquid crystals at various concentrations are shown in Fig.5 and in Table 3.

Figure 5

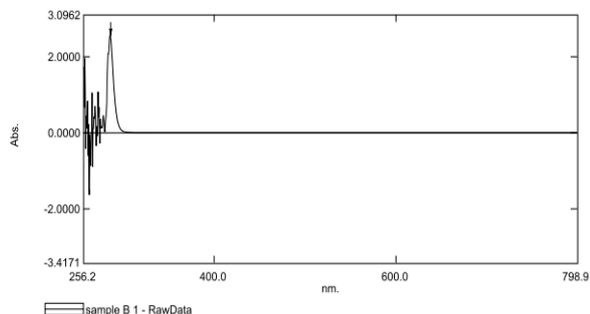


Figure 5.1: UV of Pure A

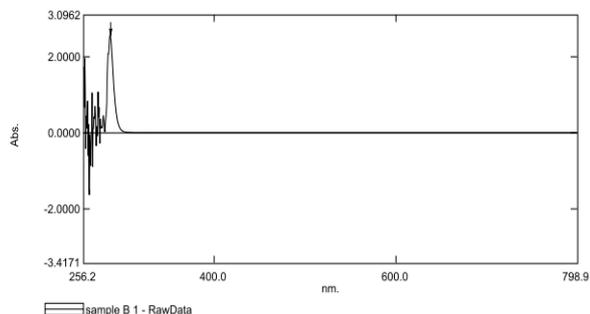


Figure 5.2: UV of Pure B

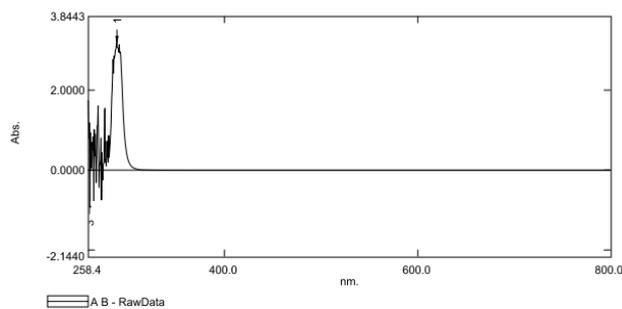


Figure 5.3: UV of A+B

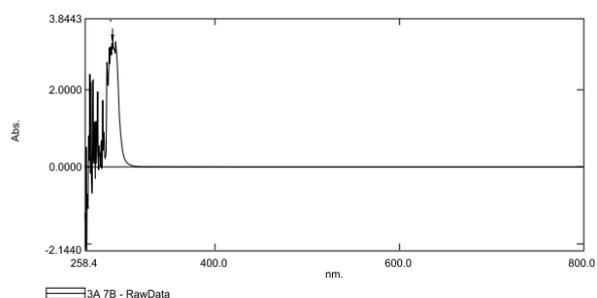


Figure 5.4: UV of 3A+7B

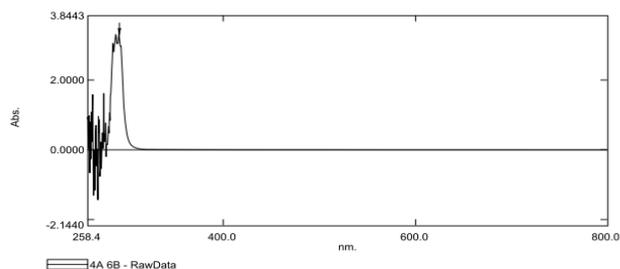


Figure 5.5: UV of 4A+6B

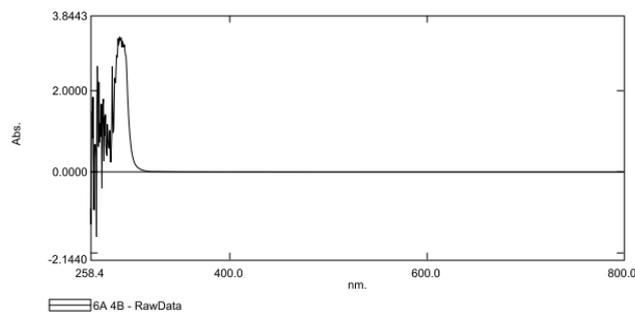


Figure 5.6: UV of 6A+4B

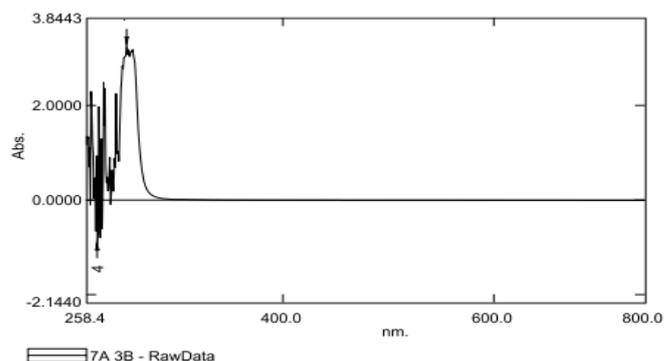


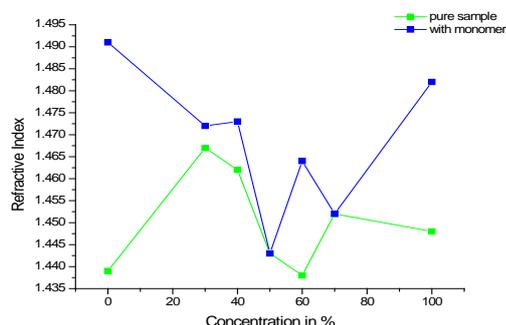
Figure 5.7: UV of 7A+3B

Table 2:

Sr. No.	Mixture at different concentrations	UV Peak
1	A(100%)	283, 206
2	B(100%)	285.5, 211.5
3	A (30%) +B (70%)	288.5, 214.5
4	A(40%) +B (60%)	291,228.5,210
5	A(50%) +B (50%)	288,237
6	A(60%) +B (40%)	256,209
7	A(70%) +B (30%)	287, 252.5

Table 3:

Sr. No.	Mixture at different concentrations	Refractive Index
1	A (100%)	1.448
2	B (100%)	1.439
3	A (30%) +B (70%)	1.467
4	A (40%) +B (60%)	1.462
5	A (50%) +B (50%)	1.443
6	A (60%) +B (40%)	1.438
7	A (70%) +B (30%)	1.452

**Figure 6:** Graph of refractive index

The R.I measured by Abbe's Refractometer of all composite liquid crystals at various concentrations at room temperature is shown in Table 3

4. Result and Discussions

Table 4: Comparison of phase transition temperature for different technique observed

Sr. No.	Mixtures at different Concentration.	FPSS	PMS	DSC
1	A (100%)	77.5, 90, 92	76	77.91, 91.49
2	B (100%)	44.4	55	45.92,
3	A (30%) +B (70%)	57	57	44.32
4	A (40%) +B (60%)	48	48	43.71
5	A (50%) +B (50%)	45	45	46.47
6	A (60%) +B (40%)	47	53	42.36
7	A (70%) +B (30%)	67	67	42.38, 68.49

Comparison of observed transition temperatures for pure sample and different concentrations are shown in the Table 4 for three techniques which are in consistency. Some common bond formations are seen for all the concentration but additional bond of NO₂- nitro compound is observed in 7A+3B composite. High concentrations of nematic liquid crystal (3A+7B) have higher value Refractive index.

5. Conclusion

The liquid crystals (LC) mixtures at various concentrations were studied. The changes were found in phase transition temperature; some concentration has been extended by 2⁰-

4⁰C and lower by 4⁰-6⁰ and confirmed by PMS and DSC/DTA. The mesomorphic phases are found in PMS study. By FTIR found the different functional groups like carboxylic acid, Aldehydes, Hydro halide, and Epoxide all over the mixtures. The occurrences new bonds were confirmed by FTIR and DTA analysis shows improvement in thermal behavior. UV-Vis spectrophotometer measures the amount of light absorbed at each wavelength of the UV and visible regions of the electromagnetic spectrum. By Refractive indices changes as a function of temperature and molar concentration made to understand the behaviour of the system by using Abbe's Refractometer. The changes in refractive index is due to change in concentration of composite liquid crystal which of can be used for optical applications.

6. Acknowledgment

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