

Thermal Analysis of Liquid Crystal Mixtures

Dr. Jyoti R. Amare

Atharva college of Engg./University Mumbai, India

Corresponding Author: Dr. Jyoti R. Amare

Abstract: The thermal behavior of mixtures formed by ferroelectric nanopowder, monomer, and nematic liquid crystal (LC) were investigated by Differential Scanning Calorimetry (DSC) and phase identified by Polarizing Microscopy (PMS). The DSC and PMS result clearly indicates that synthesized mixtures produced display liquid crystalline properties. The phase transition temperature (PTT) values obtained in DSC experiment are in line with the PMS observations. Investigation of thermal properties of mixture reveals that nematic range of synthesized mixtures is affected in a ways that is dependent different in attached moieties to the chain length on both the mixtures ratio and furthermore, the phase transition temperature values of ternary mixtures increases with increasing heating rate.

Keywords: Liquid Crystals (LCs), Polarizing Microscopy (PMS), Fabry Perot Spectroscopy (FPSS), Differential Scanning Calorimetry (DSC), Phase Transition Temperature (PTT).

I. Introduction

Liquid Crystalline state is fascinating, intriguing, mysterious, delicate fourth state of matter which shows anisotropic nature. They are characterized by high molecular orientation order in their mesomorphic states. The history of liquid crystal began with the observation by Renitzer [1]. Each mesophase of liquid crystals is a microscopically uniform intermediate state between an isotropic liquid and a crystalline solid. Broadly liquid crystal phases are of three types viz. Cholesteric, Nematic, Smectic. Some liquid crystal phases can be identified quite simply by using just one technique. However, to be more certain of the liquid crystal phase type, several different techniques are employed.

The phase transition identification of LCs and phase structure are principally based on thermal analysis, optical microscope and XRD. The thermotropic liquid crystal exhibits polymorphism upon variation of temperature. The polymorphic transformations can be studied by different techniques viz Polarizing Microscopy (PMS), Differential Scanning Calorimetry (DSC), Fabry perot Scattering Studies (FPSS). PMS is very simple and vivid method [2]. PMS reveals that each different liquid crystal has a distinct optical texture. Differential Scanning Calorimetry is used as confirmatory tool for PMS. DSC is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of the sample and reference is measured as a function of temperature. The transition between the highly structured phases is readily detectable by DSC. Fabry perot scattering studies is an analytical technique and gives information about phase transition temperatures. The Fabry-Perot interferometer is capable of extremely high resolution. It was designed by C. Fabry and A. Perot in 1899. It gives bright fringes on a dark background. The graph of temperature vs. diameter of Fabry-Perot fringes shows an abrupt variation at phase transition temperature.

The temperature sequence of the phases is given as: $Ch \leftrightarrow S_E \leftrightarrow S_B \leftrightarrow S_F \leftrightarrow S_C \leftrightarrow S_D \leftrightarrow S_A \leftrightarrow N \leftrightarrow I$

Mixtures of liquid crystal phases bring the melting point down which helps or gives wide applicability of its use in various applications. These mixtures show phase transition temperatures and other physical properties which are different from their constituents. Transition temperatures of one's choice can be achieved by mixing ratio of different liquid crystal phases. The behavior of switching time, optical response time also changes with the temperature in the mixtures. The liquid crystal mixtures can also be used to investigate interaction between order parameters in different phases. They can be used to create new phases such as chiral nematic or smectic by mixing chiral molecules in liquid crystals. Mixtures can also be used to change the pitch of the phase.

II. Experimental Methods

All the liquid crystals are purchase from Sigma-Aldrich Chemicals Pvt Limited.

Cholesteric liquid crystal: - Cholesteryl Pelargonate (CLC)

Mixtures:

1. Cholesteryl Pelargonate (CLC)+4Cynophenyl-4n-Hexyl benzoate (CLC-1)
2. Cholesteryl Pelargonate (CLC)+Cholesteryl Chloide (CLC-2) + Cholesteryl Oleate (NLC)
3. Cholesteryl Pelargonate (CLC)+Ethylene Glycol Dimethacrylate-EGDMA-Monomer (M)
4. Cholesteryl Pelargonate (CLC) + Barium Titanate-BaTiO₃- Ferroelectric Nanopowder (N)

Preparation of mixtures:

The mixtures 1 (CLC-50%+CLC-1-50%) and 2 (CLC-80%+CLC-2-15%+NLC-5%) were first weighed accurately using analytical microbalance in the required proportions. Then the mixture were stirred enough to ensure thorough and complete mixing. This homogeneous mixture was then used for the preparation of slides. The third mixture contain monomer EGDMA was dispersed in CLC by encapsulation method to form Polymer Dispersed Liquid Crystals (PDLC). EGDMA is a water insoluble difunctional methacrylic monomer employed as cross linking agent or low viscosity reactive diluent. In the fourth mixture Ferroelectric Nanopowder of Barium Titanate (BaTiO_3) was mixed with Oleic acid and Heptane in appropriate proportion by weight and then this mixture was doped with CLC by ultra-sonication method [3]. The ultra-sonication ensures homogeneous distribution of nanopowder in CLC. The mixture was kept in vacuum for six hours for complete evaporation of heptanes. The resulting sample contains the small concentration (~1%) of BaTiO_3 nanoparticles.

Preparation of sample slide:

On a clean dry piece of wafer thin glass, usually called 'cover slip' a small spec of sample under investigation was placed. It was then sandwiched between two cover slips and the sides were sealed by non conducting tape. When the sample slide is heated, at a particular temperature the sample melts and spreads uniformly between the bottom and top cover slip. The melted sample is held in place due to surface tension forces. These slides were used for texture observation as well as to determine the phase transition temperatures. Polarizing Microscopy (PMS): PMS is the most widely used method in the study of various textures and determination of phase transition temperature. Liquid crystals phases possess characteristic textures when viewed under polarized light. Heating and cooling cycles of LC mixtures were observed. Different images of LC compound were taken for every phase.

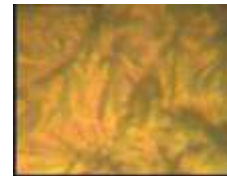
Differential Scanning Calorimetry (DSC/DTA): The phase transition temperatures were determined using DSC. It measures the temperature and heat flows associated with transitions in materials as a function of time and temperature in a controlled atmosphere. The peaks correspond to transition from solid to isotropic phase.

Fabry perot Scattering Studies (FPSS): In FPSS study we found the new phase transition temperatures. In FPSS light from monochromatic source is incident on LC. It gets scattered by the LC molecules, which fall on fabry perot etalon. The fringes obtained are in the form of circular rings. The diameter of these rings depends upon the wavelength of the light used and the angle of incidence and the thickness of the air-gap. The fringes obtained in the FP interferometer are based on the multiple reflection of beam of source.

III. Result and Discussion

The studies conducted on LC mixtures have attractive physical properties. The morphological structure of mixture was examined by PMS. The PTT in such mixture shows changes based on ratio. By PMS studies we observed the textures which are, fan like (Sm), Blue Phase 76°C (CLC), Broken fan (CLC+CLC-1), (Sm-N) Threaded Texture appeared at 45°C (heating) (CLC+CLC-2+NLC), Phase transition Nematic/ S_G Star-shaped G domain with Six fold symmetry axis (cooling) 45°C (CLC+CLC-2+NLC), Nematic Droplet (CLC+M).

1.Polarizing Microscopy (PMS): According to images observed from PMS, the phase analyses of sample were performed. The textures obtained by Polarizing Microscopic Studies during heating and cooling cycles are shown in Figure 1-8 below.

**Fig1: Fan like (CLC)****Fig2: Blue Phase 76°C (CLC)****Fig 3: Broken fan (CLC+CLC-1)****Fig 4: Nematic Threaded Texture appeared**

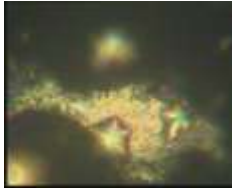


Fig 5: Phase transition Nematic/SG with Six foldsym. Axis (cooling (CLC+CLC-2+NLC)

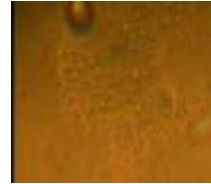


Fig 6: Nematic Droplet Star-shaped G domain

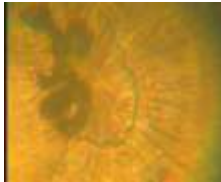


Fig 7: 79.50°C Broken fan shaped



Fig 8: 58.2 °C Nematic thread like (CLC+N)(CLC+N)

2. Differential Scanning Calorimetry (DSC/DTA): DSC/DTA graph shown in fig 9-13.

The changes in peak and ΔH value were found for CLC and their mixture. Comparative studies show that addition of nanopowder evolves maximum heat energy. In the mixtures of LC in different proportion absorbs heat energy.

Table no. 1: PTTs

Sample	ΔH (J/g)	ΔH (J/mol)	ΔS (J/mol°C)
Pure CLC	64.5	0.1031	0.00141
CLC+CLC-1	-68.50	-0.08210	-0.00176
CLC+CLC-2+NLC	-9.97	-0.00629	-0.000086
CLC+N	72.1	0.1153	0.001579

The table shows PTT, entropy changes (ΔS) and enthalpy (ΔH), it indicates the phase transition enthalpy changes during heating was lower than entropy. The PTT can be calculated by $\Delta H = T \Delta S$. Calorimetric measure values are important in assignment of phase transition. According to such values crystal solid Sm, Sm A-Nematic and N-I phase transition were first order transition.

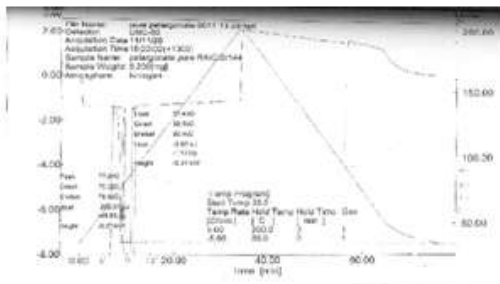


Fig 9: Graph of CLC

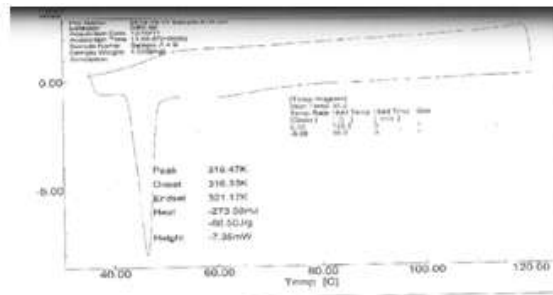


Fig 10: Graph of CLC+CLC-1

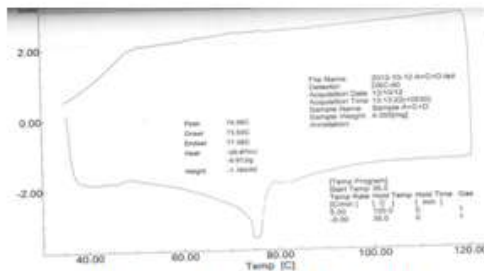


Fig 11: Graph of (CLC+CLC-2+NLC)

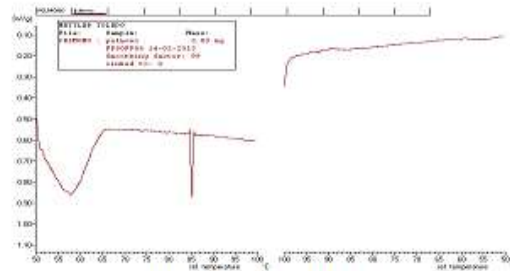


Fig 12: Graph of CLC+N

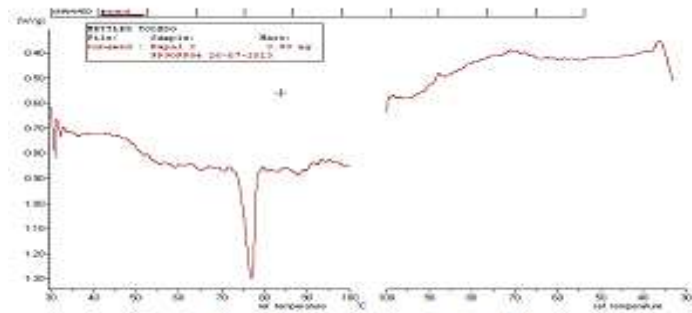


Fig 13: Graph of CLC+N

3. Fabry perot Scattering Studies (FPSS):

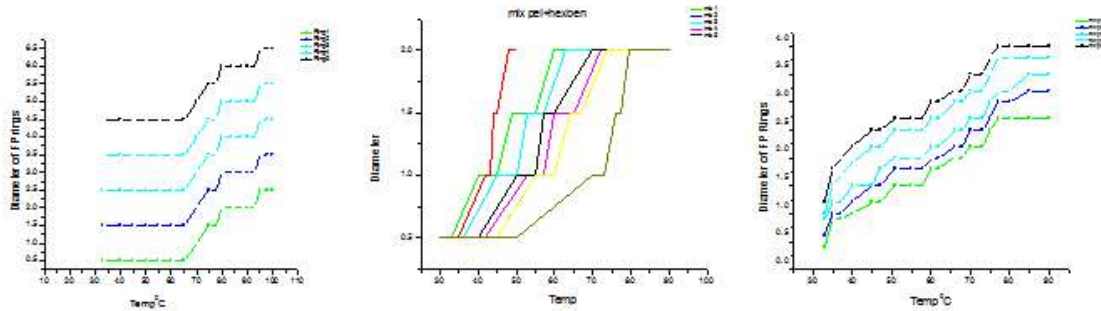


Fig 12: Phase diagrams of CLC

Fig 13: Phase diagrams of CLC+CLC1

Fig 14: Phase diagrams of CLC+CLC-2+NLC

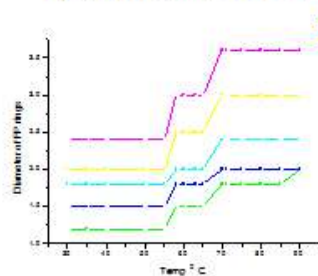


Fig 15: Phase diagrams of CLC+M

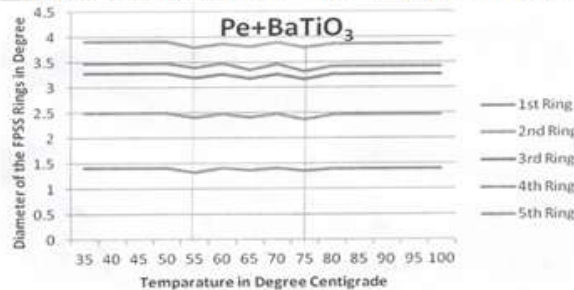


Table no. 2: Comparison of PTT'S of LC and their mixtures.

Sr. No	LC and their Mixtures	PMS	DSC/DTA	FPSS
1	CLC	76	77.91, 91.49	77.5 , 90,92
2	CLC+ CLC-1	45	46, 47	45
3	CLC+CLC-2+NLC	74	53,73	73
4	CLC+M	76	85	77.90
5	CLC+N	58.2,79.5	56,77	52,58,68,79

IV. Conclusion

The thermal behavior of liquid crystal between various mesomorphic forms in Binary, Ternary with monomer and with nanopowder was observed by DSC/DTA and FPSS. Phase transition temperature and enthalpies of mixture were specified from obtained DSC thermogram. The mesomorphic structure of mixture was examined by PMS for all the mixtures as well as for pure cholestric LC indicated the presence of different phases at different transition temperatures. Fan like texture confirmed the presence of cholestric phase (Sm) in pure CLC. The phase transition temperatures were enhanced in all the mixtures except for the mixture of CLC and 4 Cynophenyl-4n-Hexyl benzoate (CLC-1). In this mixture the phase transition temperatures of pure LC were suppressed and new transition temperatures were detected. New transition temperatures were detected in other mixtures also. We observed Blue phase for pure CLC. Blue phases are special types of liquid crystal phases that appear in the temperature range between a chiral nematic phase and an isotropic liquid phase. Blue phases have a regular three-dimensional cubic structure of defects with lattice periods of several hundred nanometers, and thus they exhibit selective Bragg reflections in the wavelength range of light (visible part of electromagnetic radiation) corresponding to the cubic lattice. DSC/DTA and FPSS were used as supportive tools

to confirm the phase transition temperatures obtained by PMS. This mixture study helps to design new LC material as per the requirement of different applications of LC.

Acknowledgments

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