Investigation of Parameters of Liquid Crystal Composite System

S.J.Gupta
Mumbai University, Physics Dept
Santacruz (E) , Mumbai, India

Balakrishna R.S.
Thakur College of Eng&Tech
Kandivali (E) Mumbai, India,

Vinita D.
N.E.S.Ratnam College, Physics Dept.
Bhandup(W)Mumbai,India

ABSTRACT
Using a number of techniques, investigations have been carried out for forty-eight different systems of sample combinations according to varying components and different concentrations of pure Liquid crystals(LCs) Cholesteryl Pelargonate (CP) as well as Composite systems formed with polymer of metha methyl acrylate (PMMA-a clear plastic) in different proportions with azobenzene dye (Orange). The Phase Transition Temperatures (PTTs) were found using the Fabry-Perot Scattering Studies (FPSS). The textures and the PTTs of pure CP have been studied using the supplementary techniques of Differential Thermal Analysis (DTA) and Polarising Microscopy Studies (PMS). The absorption of the sample in the visible range was found using Ultra-Violet visible spectroscopy (UV-VIS). The infrared absorption was also studied using Fourier Transform Infrared (FTIR) spectroscopy. The results of the above investigations are being presented here. Addition of azobenzene dye to pure CP decreased its clearing temperature from 88^0C to 62.8^0C. A comparative study between the systems, with and without azodye, showed that the addition of azobenzene dye brought about a change in the PMS textures indicating a change in the birefringence properties. Further, the clearing temperature also varied with different concentrations of PMMA in the mixture of CP + azodye; the clearing temperature was maximum (77.5^0C) for the sample which contains 80%CP+20%PMMA+1% Azodye). Results of the UV/VIS analysis, FTIR analysis are also presented and discussed in this paper.

Categories and Subject Descriptors
J2 Electronics ,Optoelectronics Liquid crystals

General Terms
Design, Experimentation and Measurements.

Keywords
Liquid Crystal Display(LCD) devices, Cholesteric LCs, Polymers, Azodyes, PTTs.

1. INTRODUCTION
Thermodynamic phases of condensed matter with a degree of order intermediate between the crystalline solid and the liquid are called *Liquid Crystal phases* or Mesophases [1]. The distinguishing characteristics of the phases are Positional order and /or Orientation order. Depending on the degree of positional order and/or orientation order, different liquid crystal phases arise:- Smectic, Cholesteric or Nematic. Each liquid crystal mesophase can form its own characteristic '*texture*' useful in the identification of the mesophase. Liquid crystals are also classified as Thermotropics, Lyotropics and Polymerics. Polymer dispersed liquid crystals (PDLCs) consist of liquid crystal droplets dispersed in the polymer matrix, using the technique of Thermally Induced Phase Separation (TIPS) [2].

2. Experimental work
Using the techniques of FPSS, DTA, PMS, UV-VIS and FTIR; investigations have been carried out for forty-eight different systems of sample combinations[Table1] [10],which are grouped under the following three categories according to varying components and concentrations.

Table 1. Sample combinations (S)

S	C.P	PMMA	Dye
P1	100	0%	-----
P2	20%	80%	-----
P3	25%	75%	-----
P4	50%	50%	-----
P5	75%	25%	-----
P6	80%	20%	-----
P7	100%	0%	1 %
P8	20%	80%	1 %
P9	50%	50%	1 %
P10	80%	20%	1 %

1) Pure sample of Cholesteryl Liquid crystal (CLC).

2) Composite system formed with the mixture of CLC and POLYMER (PMMA-a clear plastic) taken in different proportions.

3) Composite system formed with the mixture of CP, PMMA and azodye taken in different proportion [Azobenzene dye (Orange)].

The Phase Transition Temperatures (PTTs) and the Clearing Point Transition Temperatures(CPTTs) were found using the (FPSS) technique. The textures and the transition temperatures of the pure CLC have been studied using the supplementary techniques of DTA and PMS. The absorption of the sample in the visible range was found using UV/VIS spectroscopy. The infrared absorption was also studied using FTIR spectroscopy.

3. ANALYSIS AND DISCUSSION

3.1 Using FPSS, DTA and PMS,PTTs, CPTTs were measured. It is also observed that the clearing temperature changed for samples with different proportion of constituents [figure1]. The mesophase transitions from S_A* to N (Nematic) is identified by the change of texture from focal conic to thread-like. Also the phase transition point of Nematic to Isotropic(I) is identified by the disappearance of the texture at the isotropic (Clearing Point) temperature [Table2].

Table 2. PTTs of Samples with different techniques

S	**C.P**	**PMMA**	**Dye**	**T(S_A^*-N)**^{o}C	**T(N-I)** ^{o}C **CPTT**
P1	100	0%	---	77.7	88
P2	20%	80%	---	70	77
P3	25%	75%	---	74.8	87.4
P4	50%	50%	---	66	86.7
P5	75%	25%	---	71.9	76
P6	80%	20%	---	76.6	96.4
P7	100%	0%	1%	59.2	62.8
P8	20%	80%	1%	58.8	70.6
P9	50%	50%	1%	69	73
P10	80%	20%	1%	67.9	77.5

The mixture of CP and PMMA taken in different proportions retained the SmecticA*(Focal conic textures) and Nematic(Thread-like textures) phases at their respective PTTS. Additionally the Twisted Grain Boundary SmecticA***[**TGBA*] phase was observed for the composition P2: (20% CP and 80% PMMA) [8]. This was identified from the textures obtained using PMS (Model: CARL ZEISS JENA) which showed the SmecticA phase that are broken and the molecular director of the next block is twisted abruptly by a small angle. The PTTs were found to change depending on the proportion of the constituents. Lower PTTs were obtained when CP is mixed with PMMA indicating stabilizing effect of PMMA on CP as compared to the PTTs of the pure CP. The Smectic A* to Nematic PTTs and the clearing temperature of the composite system was found to be dependent on the concentration of the constituents [Table2]. The clearing temperature was found to be maximum (96.4^{0}C) for the composite system (80% CP + 20% PMMA) [Table2, P6]. The effect of adding azobenzene dye to pure CP was to reduce the clearing temperature from 88^{0}C to 62.8^{0}C [figure1, P1&P7]; [table2] also indicates that the PTT(S_A^*-N) for pure CP 77.7^{0}C which reduces to 59.2^{0}Cwhen Azodye is used to form the mixture (P7) .

3.2 **UV/VIS Analysis:-**UV-VIS is a reliable and accurate analytical laboratory assessment procedure that allows for the analysis of a substance. It measures the absorption, transmission and emission of ultraviolet and visible light wavelengths by matter. The ultraviolet band of the electromagnetic spectrum is further separated into three regions termed UV-A, UV-B and UV-C. Although not all scientists agree on the exact division of these wavelengths, UV-A is generally considered to be light with wavelengths between 320-400 nm; UV-B wavelengths are generally considered to be those between 290-320 nm; and UV-C wavelengths usually fall between 200-290 nm. Absorption of ultraviolet or visible light electromagnetic radiation causes electrons to move from lower energy levels to higher energy levels. Ultraviolet-visible absorption spectroscopy measures the absorption of ultraviolet or visible light. Because the spectrum of an atom or molecule depends on its electron energy levels, UV-VIS absorption spectra are useful for identifying unknown substances. In the preset work we have used Shimadzu UV-VIS, Model No.UV-3600 for the analysis of samples.

Pure CP has nearly 100% transmission in the range of 440nm and 600nm [figure2.5.1].

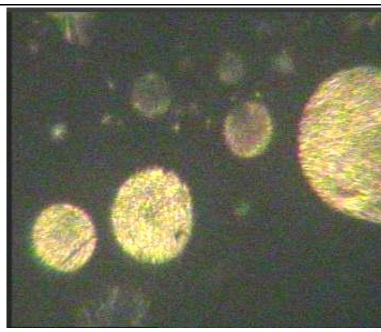
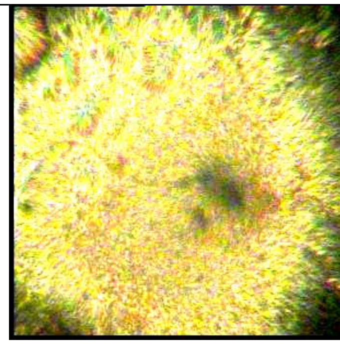
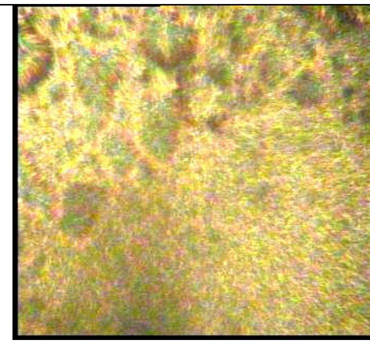
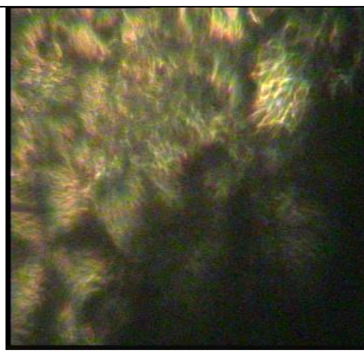
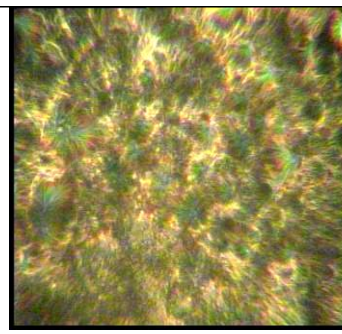
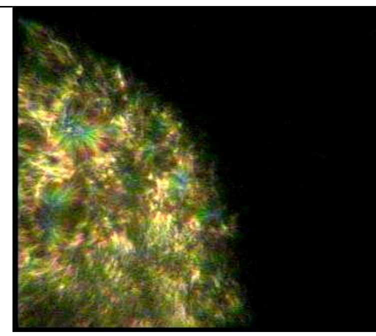
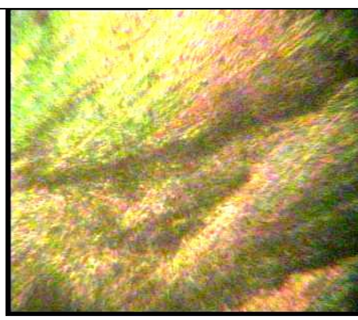
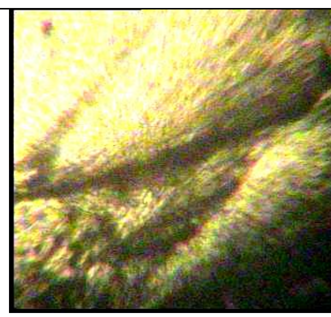
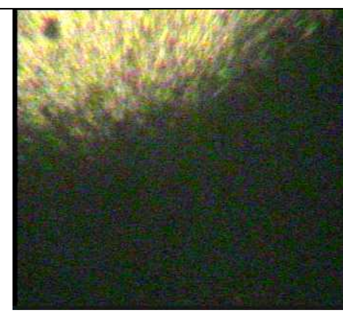
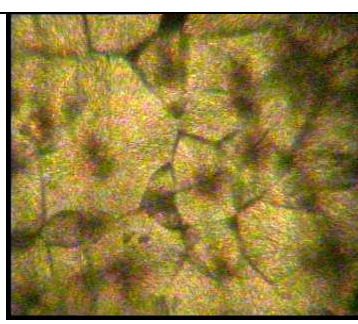
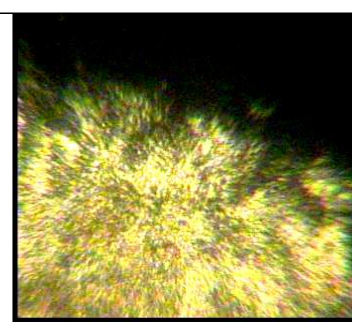
Doping CP with azobenzene dye (orange) resulted in nearly 0% transmission in the range 410nm and 480nm [figure2.5.2].

The intensity of transmission was reduced with the addition of PMMA [figure2.5.3].

It is also observed that the intensity of transmission is inversely proportion to the concentration of PMMA in the mixture [figure2.5.4]. The bandwidth peaks from 140 nm to 240nm at 2% wt/vol of CP in PMMA and drops to 170nm for 1% wt/vol of CP in PMMA, with a constant proportion of azo dye(1%).The average absorption width is found to depend upon the proportion of CP, PMMA taken for a constant proportion of azodye. At 10% transmission, the average absorption width is found to shift from 440nm to 505nm as the concentration of CP in PMMA is varied from 5% wt/vol to1%wt/vol, with a constant proportion of azodye (1%)[figure2.5.5].

3.3 FTIR Analysis:-FTIR is a standard tool for identifying types of chemical bonds in a molecule by producing an infrared absorption spectrum that is like a molecular fingerprint[7]. It is most useful for identifying chemicals that are either organic or inorganic it can be further utilized to quantify some components of unknown mixtures and also to identify the types of chemical bonds (functional group). The wavelength of light absorbed is the characteristics of the chemical bond.

FTIR analysis showed that for pure CP; a strong absorption peak was observed on the L.H.S of 3000 cm^{-1} indicating unsaturated C=C stretch and a small peak at 3500 cm^{-1} indicating –NH absorption[fig.2.6.1]. Addition of Azodye to the composite system of (CP+PMMA) leads to complete absorption of the peak on the L.H.S of 3000 cm^{-1} but a distinct small absorption peak is observed on the L.H.S of 3500cm^{-1}[fig.2.6.2]

	Figure 1. Textures obtained by P.M.S		
P1			
	53.8 ^{o}C	66.4 ^{o}C	67.1 ^{o}C
			
	70 ^{o}C	74. ^{o}C	88 ^{o}C
P2			
	30 ^{o}C	76.3 ^{o}C	77 ^{o}C
P3			
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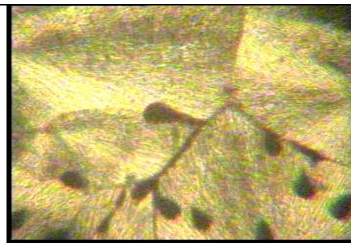
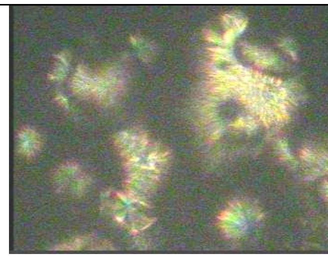
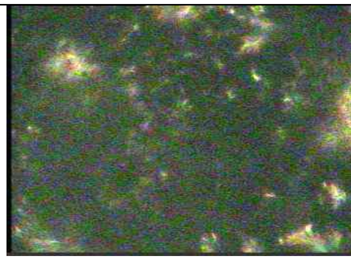
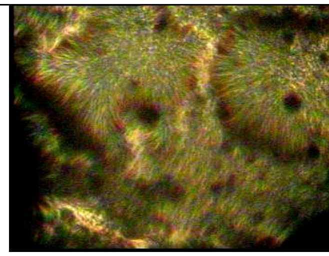
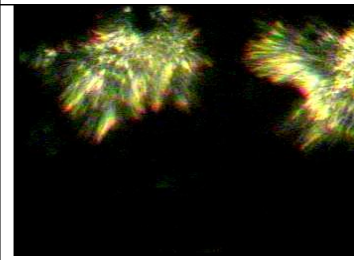
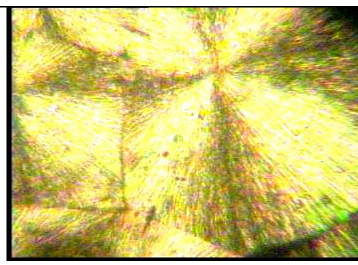
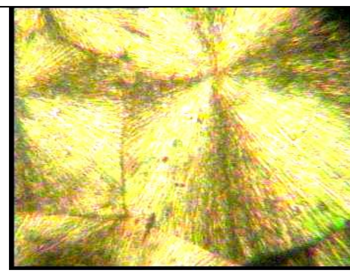
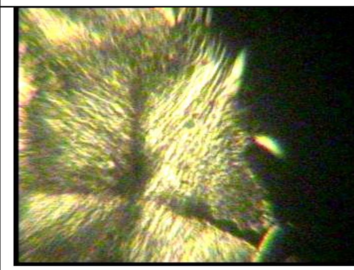
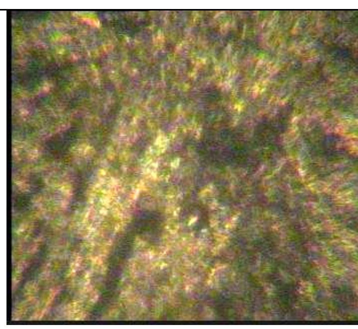
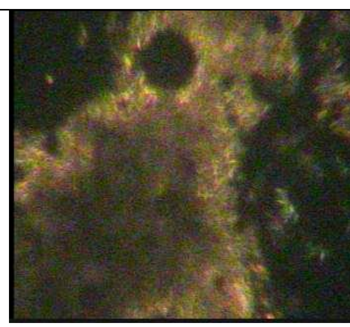
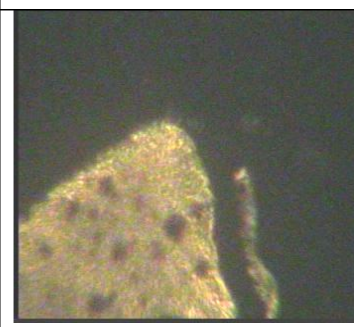
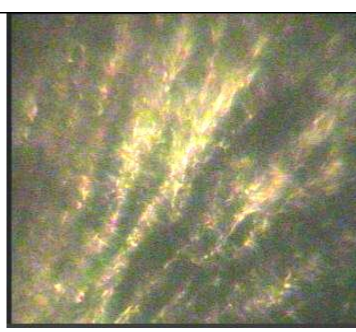
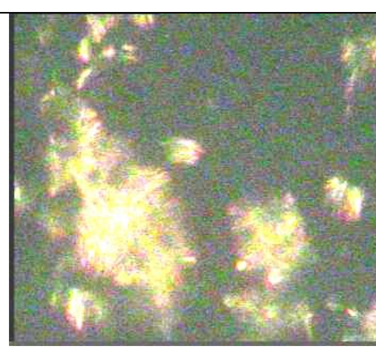
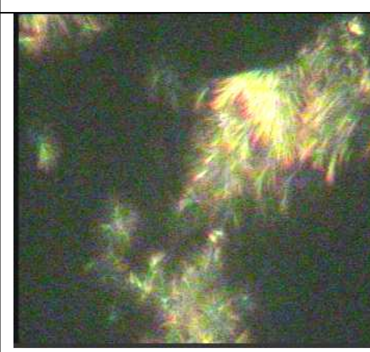
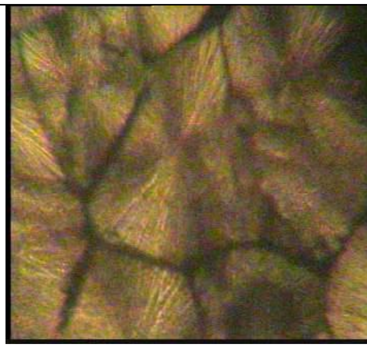
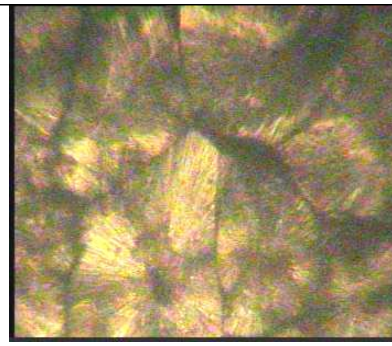
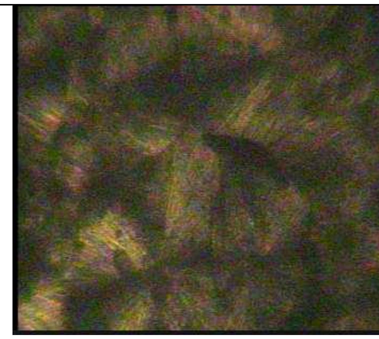
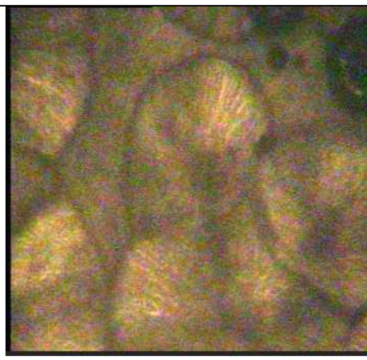
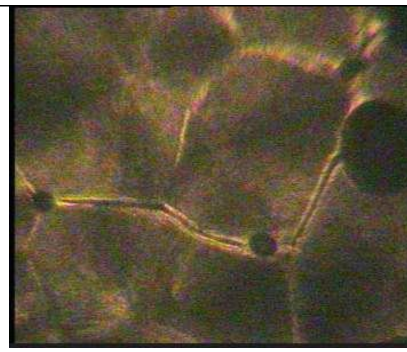
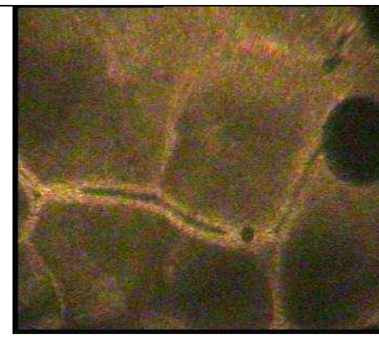
P4			
	30 ^{o}C	64 ^{o}C	78.4 ^{o}C
P5			
	30 ^{o}C	71.9 ^{o}C	75.8 ^{o}C
P6			
	30 ^{o}C	85.2 ^{o}C	96.4 ^{o}C
P7			
	30 ^{o}C	61.5 ^{o}C	62 ^{o}C
P8			

	30 °C	57.8 °C	70 °C
P9			
	30 °C	52 °C	65.4 °C
P10			
	30 °C	67.9 °C	69 °C

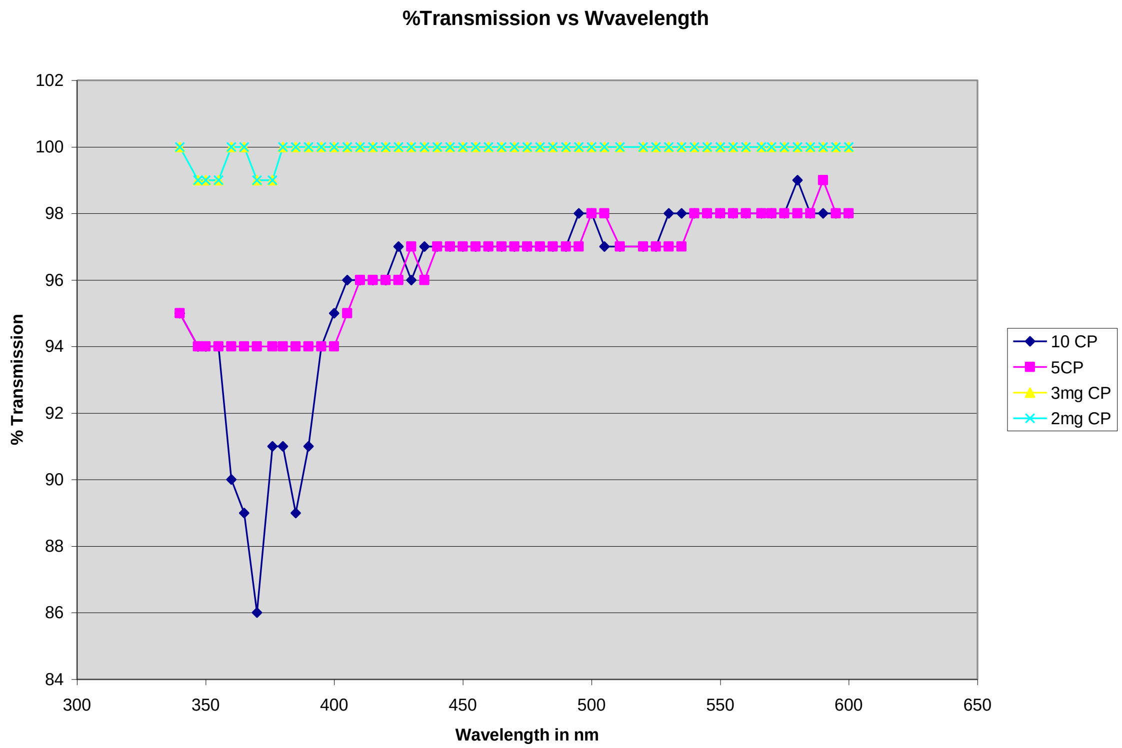


Figure 2.5.1 Transmission Vs Wavelength

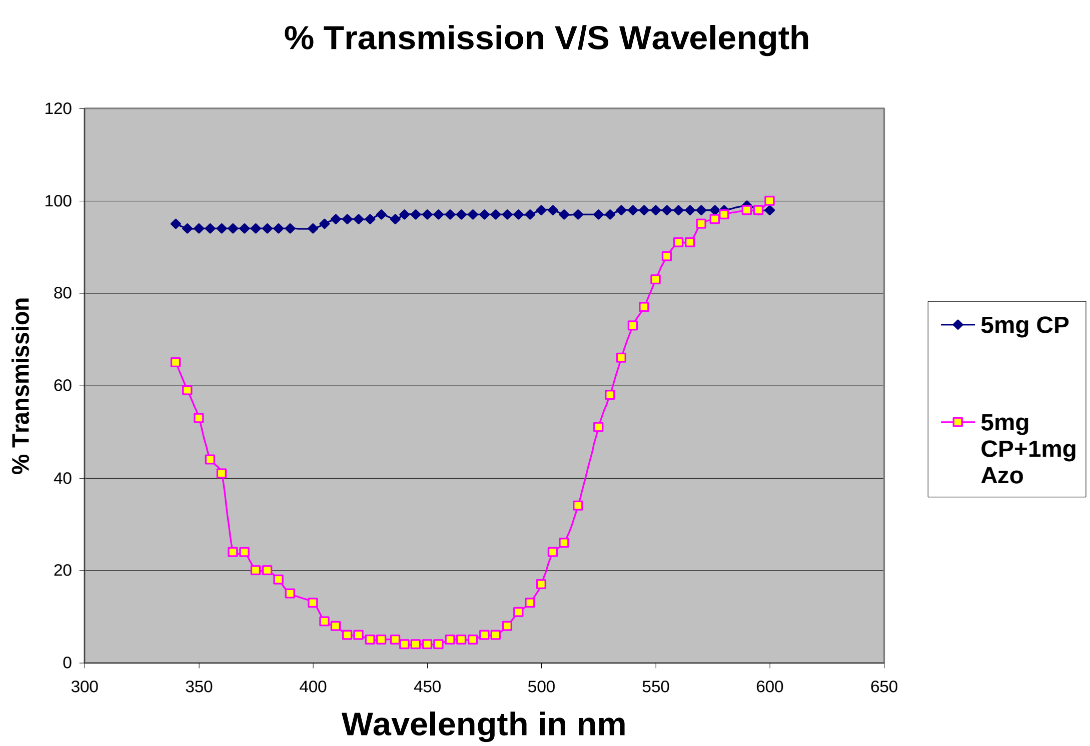


Figure2.5.2 Transmission Vs Wavelength

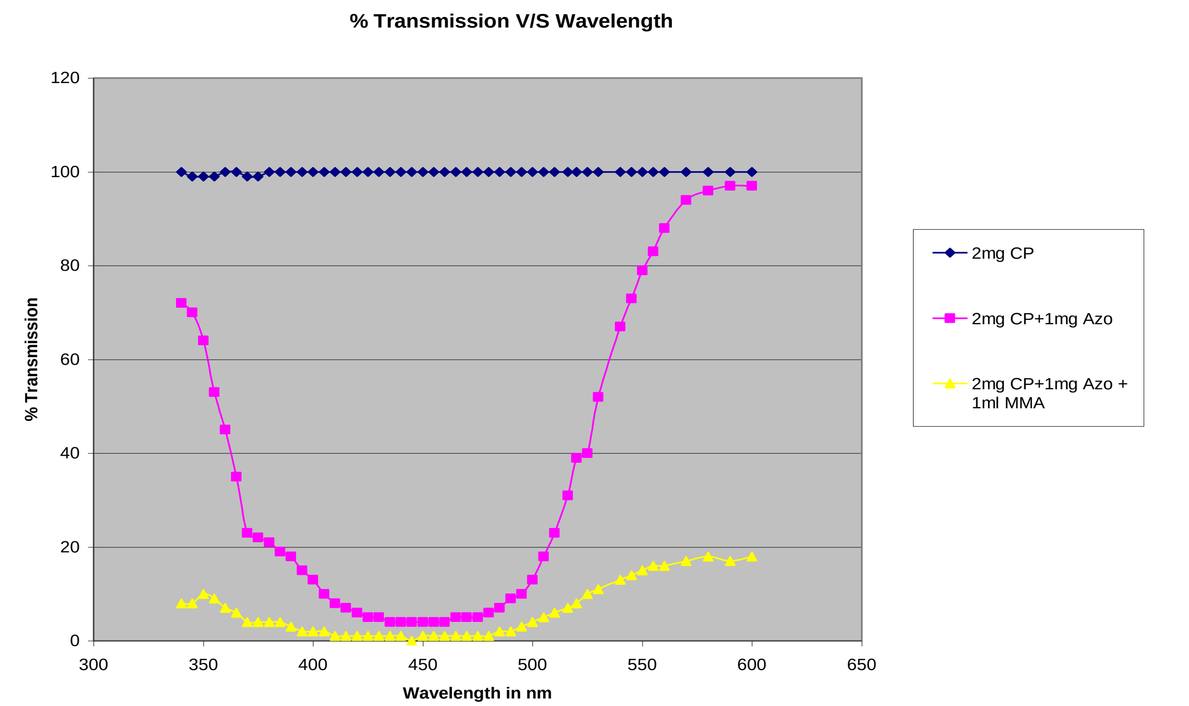


Figure 2.5.3 Transmission Vs Wavelength

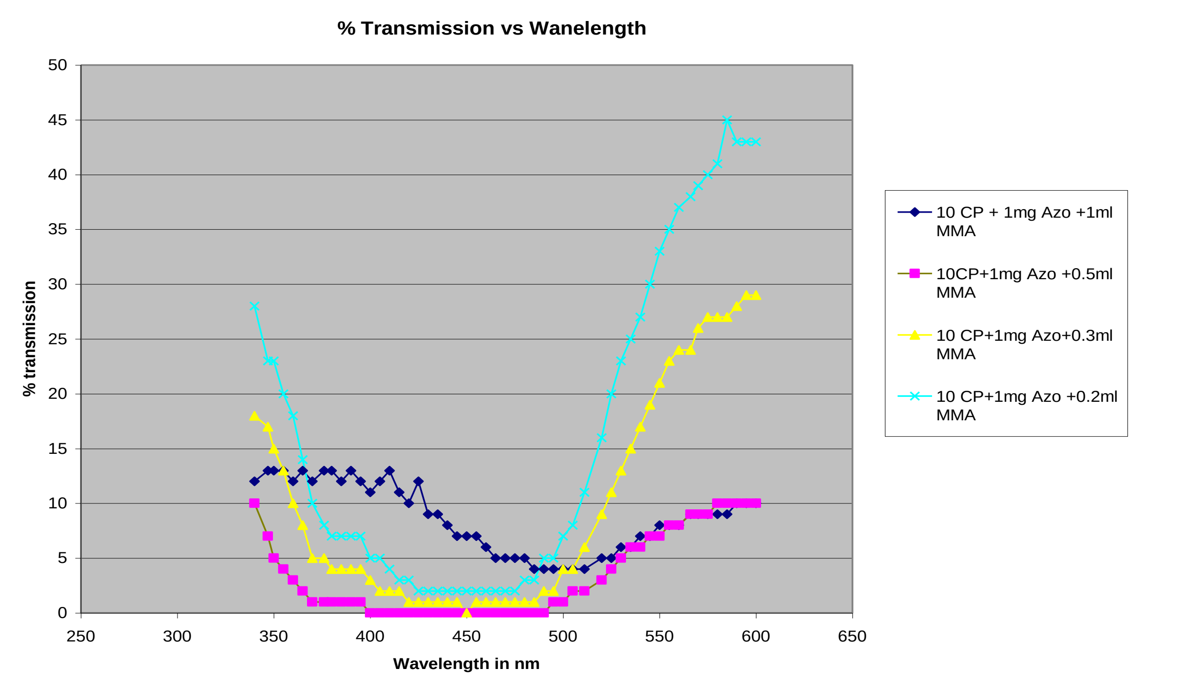


Figure 2.5.4 Transmission Vs Wavelenth

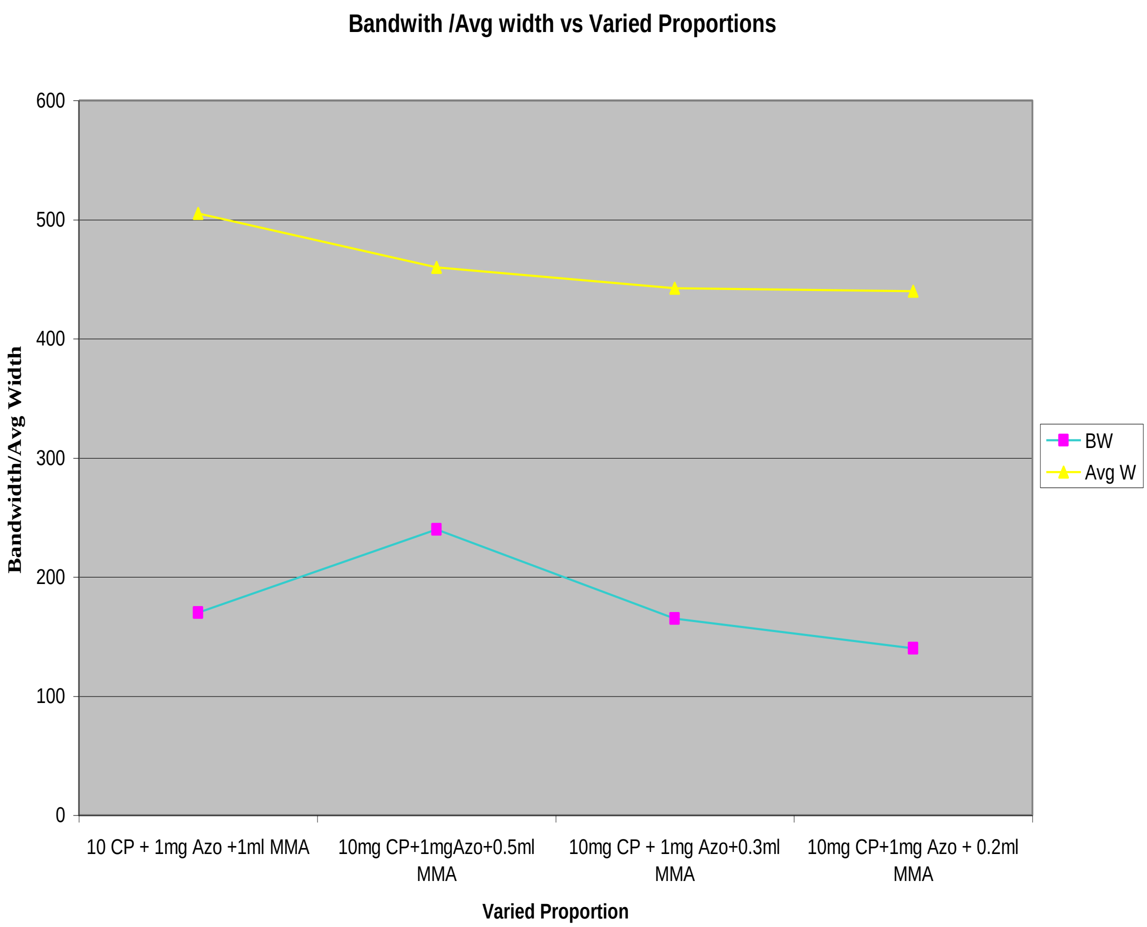


figure 2.5.5 Band width Vs Varied proportions

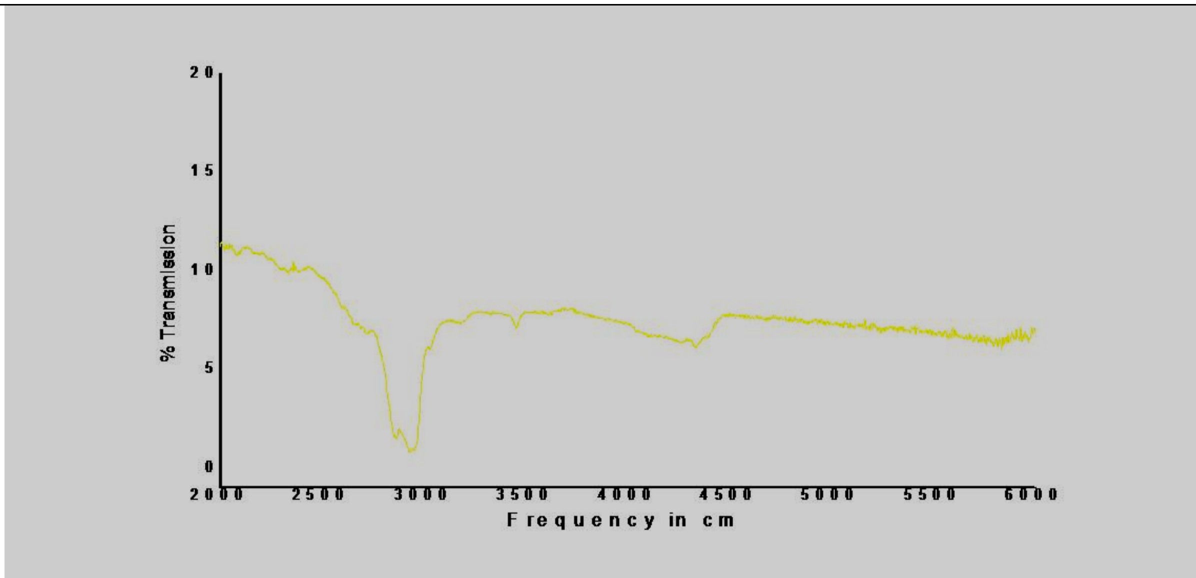


Figure2.6.1 Transmission Vs Frequency

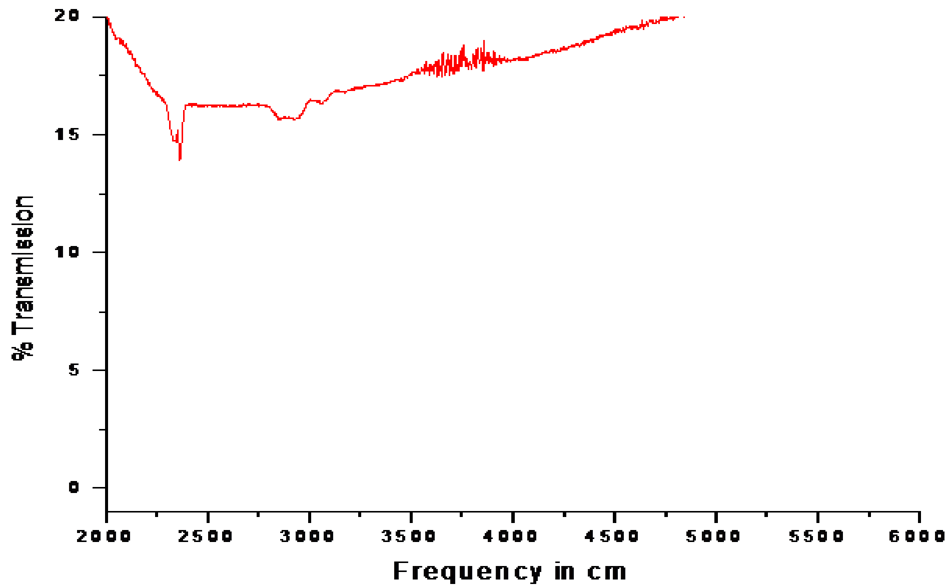


Figure2.6.2 Transmission Vs Frequency

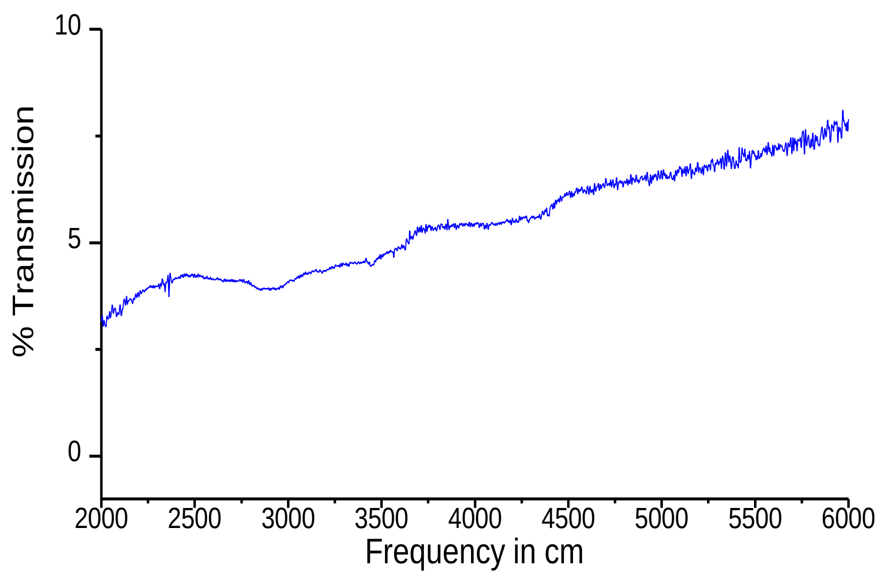


Figure2.6.3 Transmission Vs Frequency

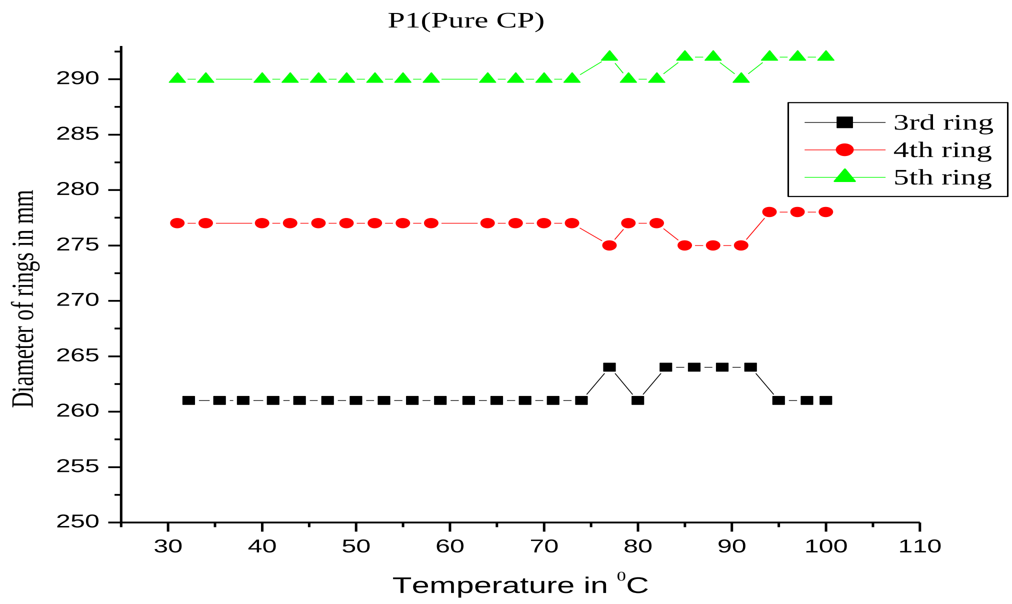


Figure2.2.1(a) Diameter of FP rings Vs Temperature

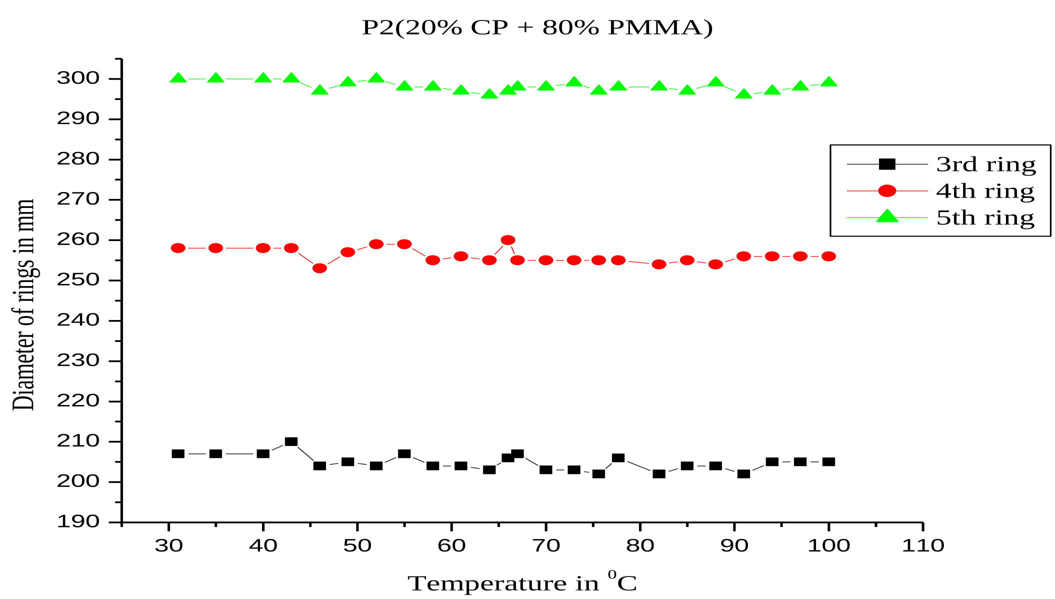


Figure2.2.1(b) Diameter of FP rings Vs Temperature

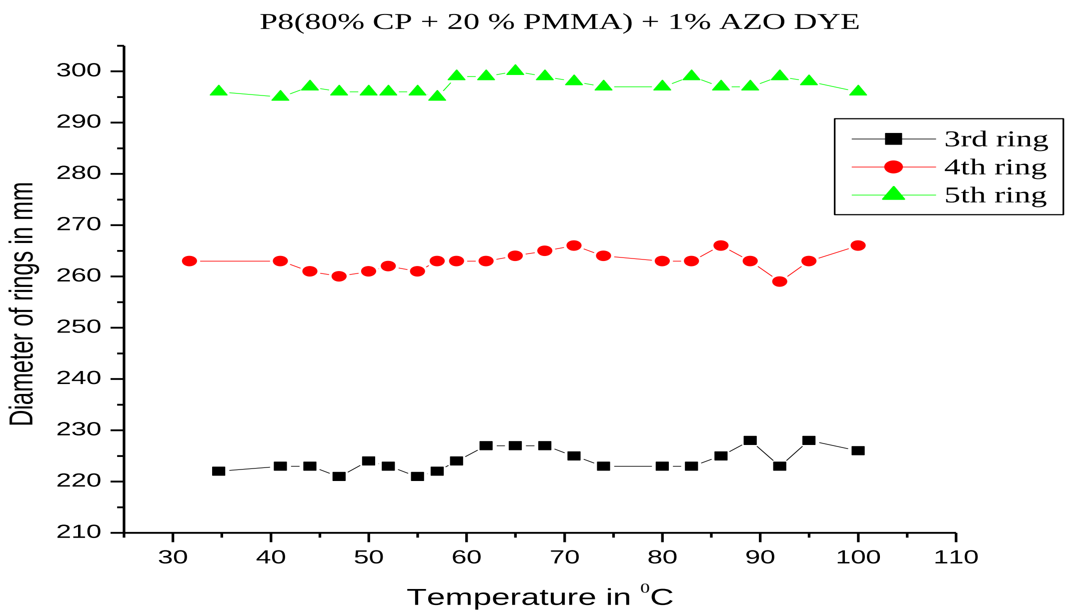


Figure2.2.1(e) Diameter of FP rings Vs Temperature

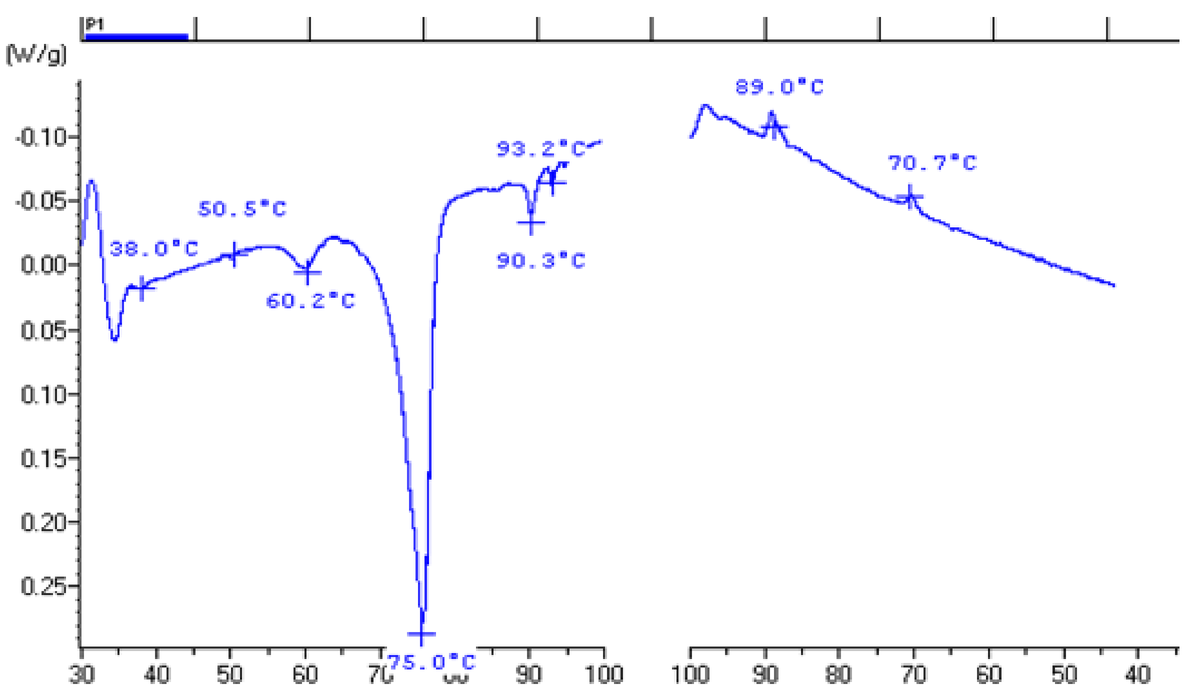


figure 2.8.1 thermo graph P1

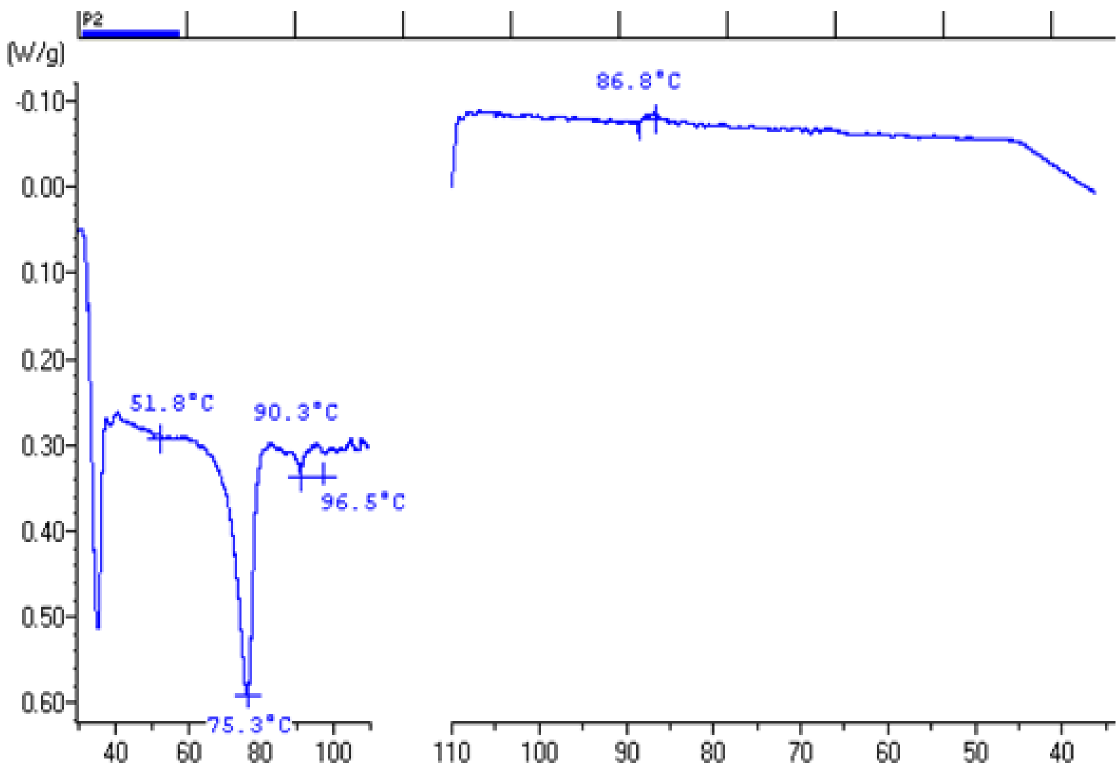


Figure 2.8.1(b) Thermo graph for sample P2

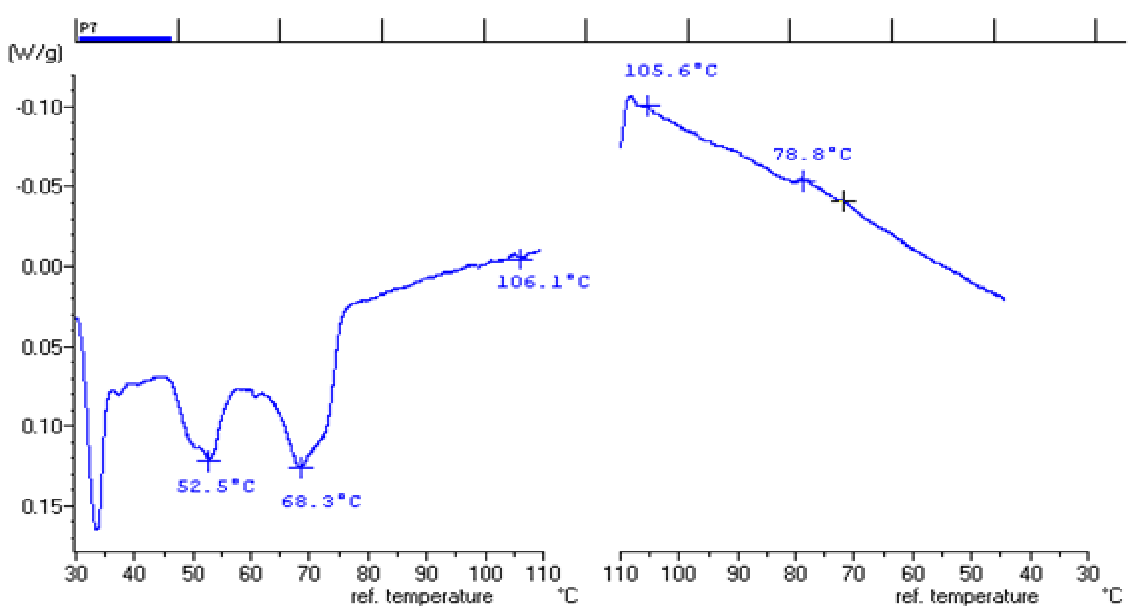


Figure 2.8.1 (d)Thermo graph for sample P9

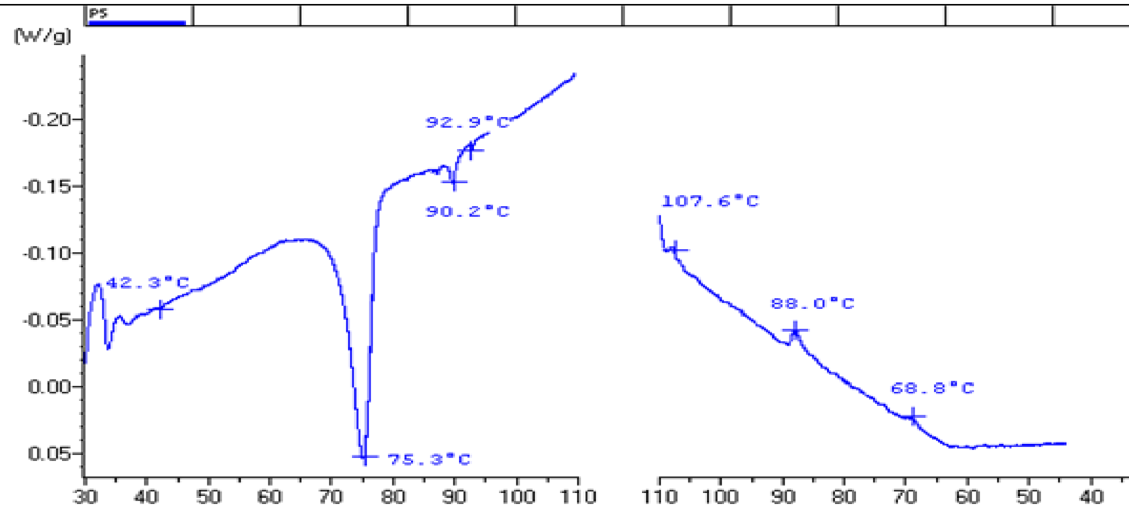


Figure 2.8.1(c) Thermo graph for sample P7

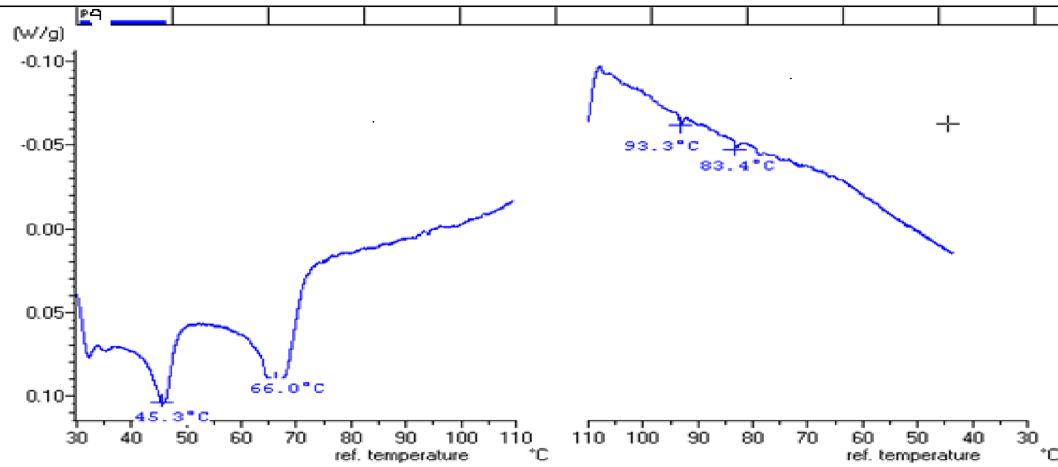
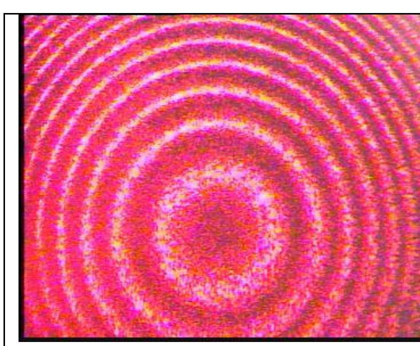
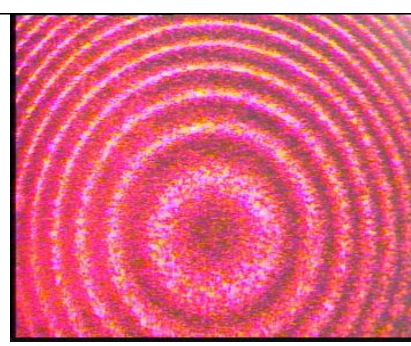
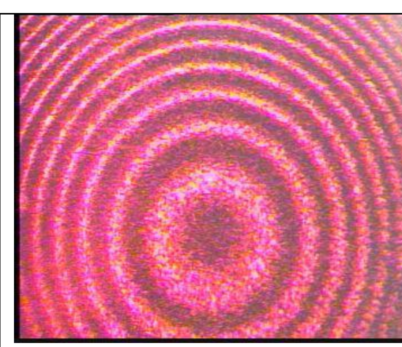


Figure 2.8.1 (e)Thermo graph for sample P8

Table2. 1FPSS fringes at different temperatures or sample P2

 i) 31 ºC	 ii) 64 ºC	 iii) 77 ºC

3.4 FPSS Analysis :- Fabry Perot Scattering System is an indigenous method developed by Prof. Gupta Sureshchandra J. Dept. of Physics, University of Mumbai. This method is useful in precisely detecting the Phase Transition Temperatures (PTTs). It is highly sensitive enough to identify PTTs not detected earlier with routine techniques. It is also economical compared to other contemporary techniques like PMS, DTA etc. The experimental set-up consist of a Fabry-Perot Etalon coupled with the spectrometer telescope, a low power He-Ne laser(wavelength 632.8nm of 5mw power) as an optical source, an infra-red thermometer to remotely sense and record the temperature of the sample, an A.C source to regulate the temperature of the sample. The diameter of the FP rings are recorded as a function of temperature and plotted[4] [5]. The graph shows abrupt changes in the diameter of the FP rings indicating the PTTS and giving CPTTs in agreement with those obtained by PMS ,DTA etc. [Table3.P2] [3].

3.5 D.T.A of the samples

DTA may be defined formally as a technique for recording the difference in temperature between a substance and a reference material against either time or temperature as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate[9].

DTA involves heating or cooling a test sample and an inert reference under identical conditions, while recording any temperature difference between the sample and reference. This differential temperature is then plotted against time, or against temperature.

In general, there are two types of phase transitions, discontinuous and continuous (sometimes called first order and second order respectively) . In order to understand the difference let us briefly consider, the thermodynamics of the phase transitions. The Gibbs free energy (G) is defined as

$$G = H - TS$$

where H is the enthalpy, T is the absolute temperature and S is the entropy. The first derivative of G with respect to T gives the negative of the entropy:

$$\frac{dG}{dT} = -S$$

The second derivative is related to the heat capacity at constant pressure.

$$\frac{d^2G}{dt^2} = -\frac{C_P}{T}$$

If the entropy at a phase transition shows a discontinuity, then a discontinuous (first order) phase transition has occurred. However, phase transitions can occur without a change in entropy and enthalpy. In such cases there is a discontinuity in the second derivative and a continuous (second order) phase transition has occurred[1] [4]. Most liquid crystal to liquid crystal transitions are discontinuous but some transitions (viz smecticC to smecticA) are often continuous. Such continuous phase transitions are revealed by a slight inflection in the baseline on the graph rather than a peak which is seen for a discontinuous phase transitions [6]. If a phase transition has been while using other techniques such as PMS, it can be revealed by DTA. Here we are also presenting the DTA curves of the above samples [table3] however in this manuscript showing only the thermo graph of sample P_1

4. APPLICATIONS

A liquid crystal is an organic compound whose properties appear to be fluid and crystalline simultaneously. Liquid crystals behave uniquely because they have several distinct optical properties which exhibit interesting changes when subjected to thermal, electric, and magnetic fields.

Liquid crystal technology has had a major effect on many areas of science and engineering, as well as device technology. Applications for this special kind of material (when mixed with other LCs, polymers, nanoparticles, nanotubes) are still being discovered and continue to provide effective solutions to many different problems of thermal effects, visibility and material strength.

4.1 *Liquid Crystal Displays*

The most common application of liquid crystal technology is liquid crystal displays (LCDs.) This field has grown into a multi-billion dollar industry, and many significant scientific and engineering discoveries are taking place.

4.2 *Liquid Crystal Thermometers*

Chiral nematic (cholesteric) liquid crystals reflect light with a wavelength equal to the pitch. Because the pitch is dependent upon temperature, the color reflected is also dependent upon temperature. Liquid crystals make it possible to accurately gauge temperature just by looking at the colour of the thermometer. By mixing different compounds, a device for practically any temperature range can be built.

4.3 Mood Rings

The meanings associated with the mood jewelery sample comes from the different temperatures your body has when you are in different moods, eg. If you are excited your body temperature may be higher than normal meaning the ring would heat up and change color. More important and practical applications have been developed in such diverse areas as medicine and electronics. Special liquid crystal devices can be attached to the skin to show a "map" of temperatures. This is useful because often physical problems, such as tumors, have a different temperature than the surrounding tissue.

The temperature sensing and color changing abilities of liquid crystals make them suitable for use in a wide range of thermometers and novelty applications. Liquid crystal colors can change through the visible color spectrum with a temperature change of only two degrees. Through dopping, the temperature range can be expanded.

4.4 *Optical Imaging*

An application of liquid crystals that is only now being explored is optical imaging and recording. In this technology, a liquid crystal cell is placed between two layers of photoconductor. Light is applied to the photoconductor, which increases the material's conductivity. This causes an electric field to develop in the liquid crystal corresponding to the intensity of the light. The electric pattern can be transmitted by an electrode, which enables the image to be recorded. This technology is still being developed and is one of the most promising areas of liquid crystal research.

4.5 *Cosmetic products*

For liquid crystal applications, high chemical purity and extremely low residual solvent impurities are essential. These materials are natural products, non-toxic and may safely be applied to the skin. Cholesteric liquid crystals are used extensively in cosmetic products to provide a shining, shimmering appearance and creamy texture, in lip gloss and skin moisturizers.

4.6 Polymer-dispersed LCDs

Polymer-dispersed displays are very bright because polarizers are not needed. Also, they are easy to manufacture since the exact thickness of the film is not important.

Twisted nematic displays (Cholesteric liquid crystal) rotate the director of the liquid crystal by 90^0, but super-twisted nematic displays employ up to a 270^0 rotation. This extra rotation gives the crystal a much steeper voltage-brightness response curve and also widens the angle at which the display can be viewed before losing much contrast. With the sharper response, it is possible to achieve higher contrast with the same voltage selection ratio. Therefore, the degree to which multiplexing is possible is greatly increased.

As new properties and types of liquid crystals are investigated and researched, these materials are sure to gain increasing importance in industrial and scientific applications

5. Results and Conclusions

Comparison of PTTs at a Glance for some samples obtained by FPSS, DTA and PMS techniques.

Table3. PTTs comparison

S	C.P	PMMA	PMS	DTA	FPSS
P1	100%	----	53.8,66. 70,77.7, 88.0	50.5,60.2, 75.0,90.3, 93.2	75.0,77.5, 81.0,89.0, 92
P2	20%	80%	69.7,75,78.0, 81.5, 87.4	51.8,75.3,90. 3,96.5	46.0,55.0 67.0,77.7, 82.0, 91.0
P4	50%	50%	61.4,78.4	56.8,76.2, 89.8	43.0,55.0, 66.0,73.0 77.7,82.0, 87.0
P6	80%	20%	67.0,77.0, 82.0,96.4	41.8,75.8, 90.5	47.0,68.0, 77.0,89.0, 95.0

TGBA* phase has been reported for the mixture (20% CP and 80% PMMA) as well as for the composite system (20% CP + 80% PMMA and 1% azo dye). The transition temperatures were found to change depending on the proportion of CP and PMMA taken The SmecticA* to Nematic transition temperature and the clearing temperature of the composite system was found to be dependent on the concentration of the constituents. The clearing temperature was found to be maximum (96.4^0C) for the composite system (P6-80% CP + 20% PMMA) .

The effect of adding azo benzene dye to pure CP was to reduce the clearing temperature from 88^0C to 62.8^0C. A comparative study between the systems, with and without azo dye, showed that the addition of azo benzene dye changed the textures indicating a change in the birefringence. Also the clearing temperature changed for different concentrations of PMMA added to the mixture of CP + azo dye**.** The clearing temperature was maximum (77.5^0C) for the sample P10 (80% CP + 20 % PMMA + 1 % Azodye)

By the UV/VIS analysis, the average absorption width is found to depend upon the proportion of the constituents

FTIR analysis showed that for pure CP, a strong Absorption peak was observed on the L.H.S of 3000cm^{-1} indicating unsaturated C=C stretch and a small peak at 3500cm^{-1} indicating –NH absorption. Addition of Azo dye to the composite system of (CP + MMA) leads to complete absorption of the peak on the L.H.S of 3000cm^{-1} but a distinct small absorption peak is observed on the L.H.S of 3500cm^{-1}.

5.*1 New Findings*

A comparative study between the systems, with and without azodye, showed that the addition of azobenzene dye brought about a change in the PMS textures indicating a change in the birefringence properties. Further, the clearing point temperature also varied with different concentrations of PMMA in the mixture of CP+azodye; the clearing point temperature was maximum (77.5^0C) for the sample which contains 80%CP+20%PMMA+1% Azodye).

5.2 *Future projections*

We envisage variations in the mesophases and the clearing point temperatures by doping these composite systems with nanoparticles and multi walled carbon nanotubes of varying dimensions. Preliminary investigations to this effect are under way in our lab with encouraging observations.

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