Binary Mixtures of PDLC Doped with Nanoparticles and MWCNT

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ABSTRACT
Using a number of techniques, investigations have been carried out for different systems of sample combinations according to varying components and different concentrations of polymer dispersed liquid crystal (PDLC) (Cholesteryl Pelargonate (CP)+ polymer of methyl metha acrylate (PMMA)) in different proportions with ZnO, Fe_2O_3 nanoparticles and Multi walled carbon nano tubes(CNT). 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 Polarizing Microscopy Studies (PMS). The results of the above investigations are being presented here. A comparative study between the systems has done; with the addition of ZnO, Fe_2O_3 showed that a change in the PMS textures indicating a change in the birefringence properties. Further, the clearing temperature also varied with different concentrations of ZnO, Fe_2O_3 in the mixture of CP + PMMA; the clearing temperature was fluctuating with increasing concentrations of doping particles (ZnO, Fe_2O_3). 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.

Categories and Subject Descriptors
Advanced computer applications(liquid crystal displays)

General Terms
Design, Experimentation and Measurements.

Keywords
Liquid Crystal Display(LCD) devices, Cholesteric LCs, Polymers, Azodyes, PMS FPSS DTA 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 . 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. Experimental work
Using the techniques of FPSS, DTA, PMS, UV-VIS and FTIR; investigations have been carried out for different systems of sample combinations

2.1 Proportional sample mixtures

2.1.1.Sample I-Undoped PDLC

1) S1=(80% of CP + 20% of PMMA)100%

2.1.2 Sample II- PDLC doped with MWCNT in following proportions.

1) 99.99% S1+0.01%MWCNT
2) 99.97% S1+0.03%MWCNT
3) 99.95% S1+0.05%MWCNT
4) 99.95% S1+0.07%MWCNT

2.1.3 Sample III- PDLC doped with ZnO in following proportions.

1) 99.8% S1+0.2%ZnO
2) 99.5% S1+0.5% ZnO
3) 99.2% S1+0.8% ZnO
4) 99.0% S1+1% ZnO

2.1.4 Sample IV- PDLC doped with $Fe_2O_3\gamma$ in following proportions.

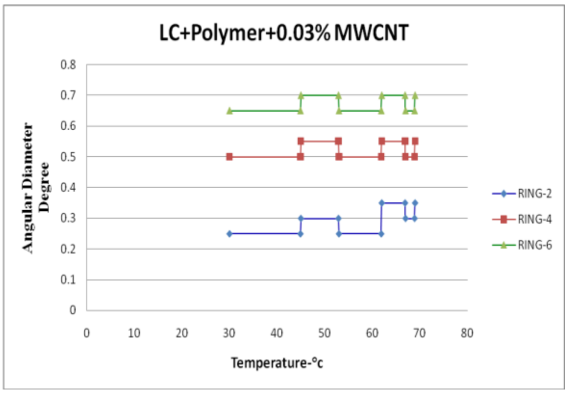
1) 99.99% S1+0.01% Fe_2O_3 γ
2) 99.97% S1+0.03% Fe_2O_3 γ
3) 99.95% S1+0.05% Fe_2O_3 γ
4) 99.95% S1+0.07% Fe_2O_3 γ

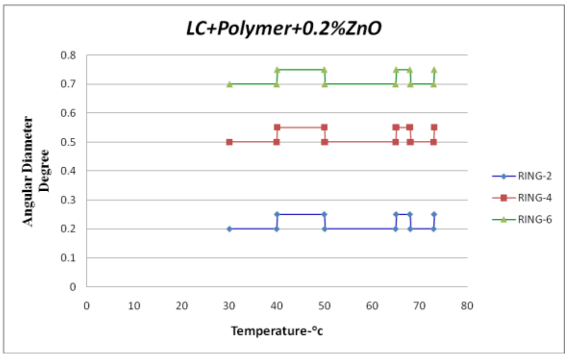
The Phase Transition Temperatures (PTTs) and the Clearing Point Transition Temperatures (CPTTs) were found using the (FPSS) technique. The textures and the transition temperatures of the samples have been studied using the supplementary techniques of PMS and DTA. The absorption of the sample in the visible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

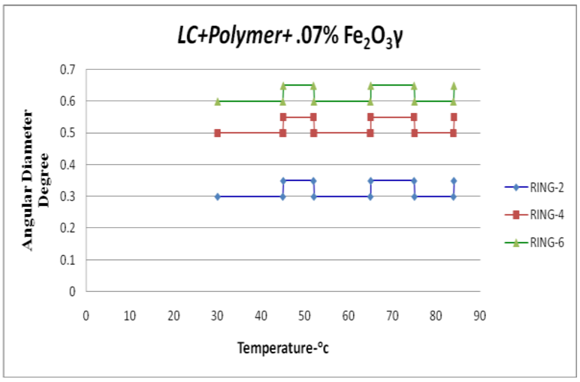
3. Observations

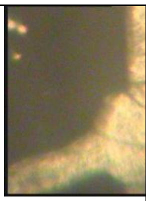
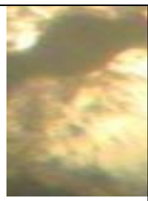
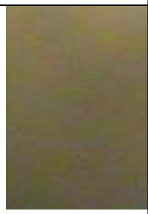
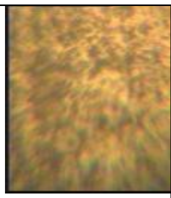
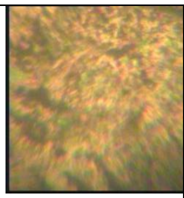
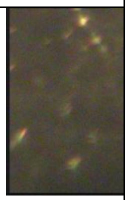
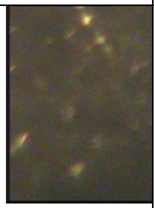
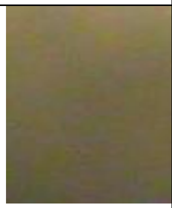
3.1 Textures/observations and graphs using various experimental techniques

3.1.1 FPSS graphs





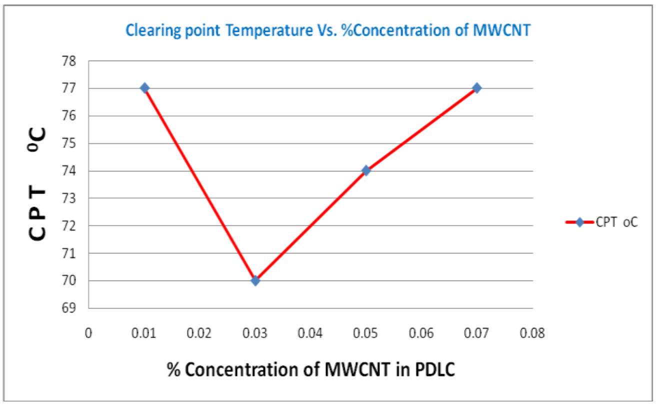


4	S1+0.03 %MWCNT			
				
	50 ^{0}C	55 ^{0}C	61 ^{0}C	64 ^{0}C
				
	66 ^{0}C	70 ^{0}C*		
5	S1+0.05%MWCNT			
				
	50 ^{0}C	58 ^{0}C	60 ^{0}C	65 ^{0}C
				
	66 ^{0}C	74 ^{0}C*		

3.1.2 PMS Textures

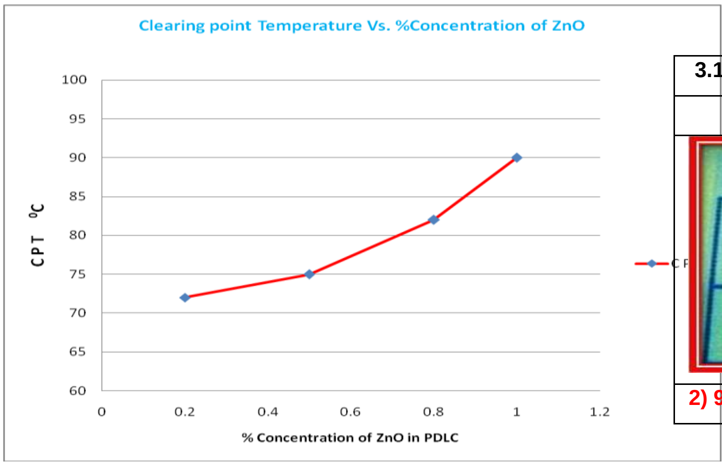
3.1.2.1 Results for Clearing point Temperature Vs. %Concentration of MWCNT.

Sr. No	% Concentration of MWCNT in PDLC	CPT ^{o}C
1	0.01	77
2	0.03	70
3	0.05	74
4	0.07	77



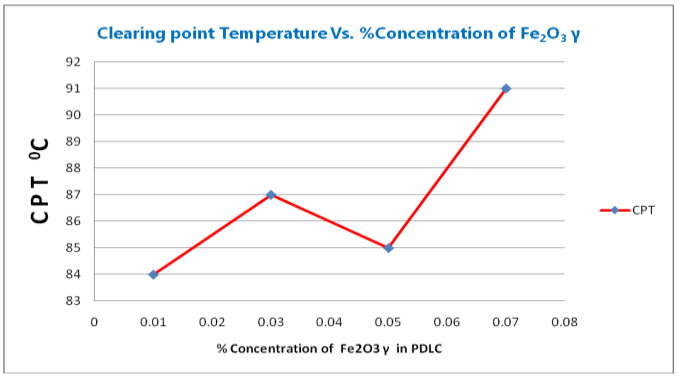
3.1.2.2 Results for Clearing point Temperature Vs. %Concentration of ZnO.

Sr. No	% Concentration of ZnO in PDLC	Clearing point Temperature in °C
1	0.2	72
2	0.5	75
3	0.8	82
4	1	90



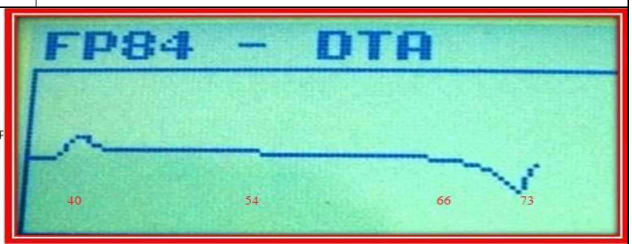
3.1.2.3 Results for Clearing point Temperature Vs. %Concentration of Fe_2O_3 γ

Sr. No	% Concentration of Fe_2O_3 γ in PDLC	Clearing point Temperature in °C
1	0.01	84
2	0.03	87
3	0.05	85
4	0.07	91



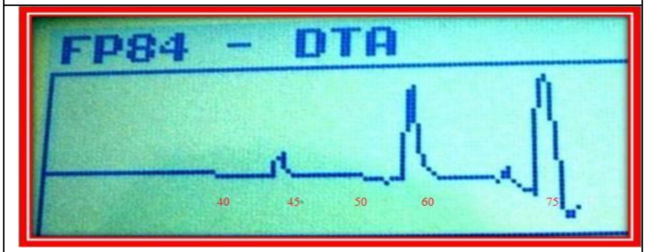
3.1.3 DTA THERMOGRAMS

1) 99.99% S1+0.01%MWCNT



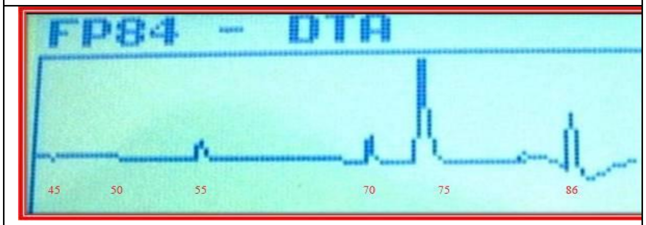
2) 99.97% S1+0.03%MWCNT

2) 99.5% S1+0.5% ZnO



3) 99.2% S1+0.8% ZnO

99.97% S1+0.03% Fe_2O_3 γ



Results of PTTS

Comparison of Phase Transition Temperatures(PTTs) using *FPSS-PMS and DTA techniques.*

Using the various techniques described earlier, the phase transition temperature [PTTs] and the Clearing Point temperature[CPTs] were obtained from the analysis of the textures, graphs, thermograms etc. attached after the tabulations. These are listed below for the samples/mixtures of LC, Polymer and ZnO,Fe_2O_3 γ , MWCNT . It is to be noted that sample S1=80% of CP + 20% of PMMA was found to be the optimum eutectic composition experimentally.

1) LC+Polymer(80% of CP + 20% of PMMA=S1)

Sample	**FPSS ^{o}C)**	**PMS ^{o}C)**	**DTA ^{o}C**
S1	47.0,68.0,77.0,89.0, 95.0	67,77,82,96 *	41.8,75.8,90.5

2) LC+Polymer+MWCNT [S1+MWCNT]

% Conc. of MWCNT.	**FPSS ^{o}C**	**PMS ^{o}C**	**DTA ^{o}C**
0.01	45,49,55,59 ,63,66,71,7 6	55,60,65,70,77 *	56,66,69,75*
0.03	45,53,62,67 ,69	50,55,61,64,66, 70*	53,64,66,70*
0.05	45,52,56,62 ,67,70	50,58,60,65,70, 74*	45 ,50,60,63, 73
0.07	43,55,66,68	50 55,60,65,77*	55,59,65*

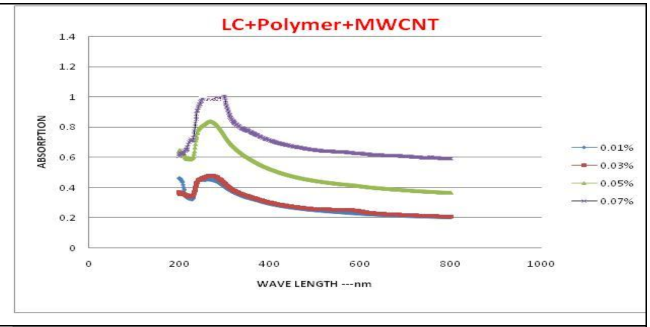
3) LC+Polymer+ ZnO [S1+ZnO]

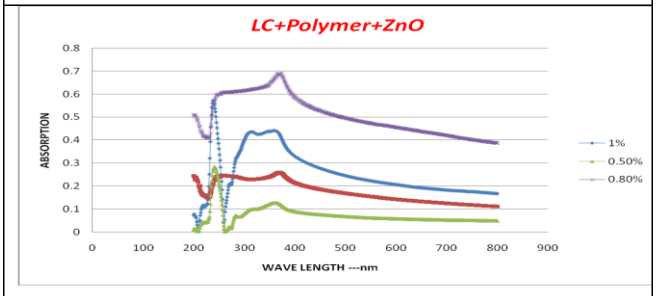
% Conc of ZnO	**FPSS ^{o}C**	**PMS ^{o}C**	**DTA ^{o}C**
0.2	40,50,65,68 ,73	40,48,57,65,69, 72*	40,50,57,65,7 4
0.5	40,55,65,75	40,45,55,67,75 *	40,45,60,72,7 5
0.8	40,55,65,76 *	45,56,66,68,74, 82*	40,60,75,80
1	60,70,85,92	60,66,70,75,87, 90*	40,45,60,77, 87*

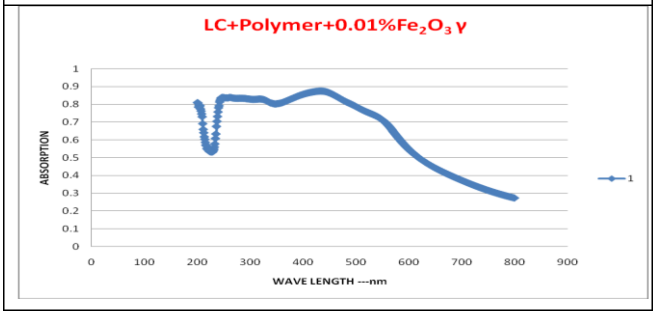
4) LC+Polymer+ Fe_2O_3 γ [S1+ Fe_2O_3 γ]

% Conc of Fe_2O_3 γ	FPSS(PTT in ^{o}C)	PMS(PTT in ^{o}C)	DTA (PTT in ^{o}C)
0.01	45 52,64,75,84	48,53,55, 63,83 84*	45,60,70,73,7 5,78, 80,82,84*
0.03	45,55,60,65,73, 84,86	52,56,61, 75,85,87*	49,50,55,75,8 6*
0.05	45,52,56,63,72, 84	50,55,62, 70,75,83, 85*,	45,63,82,85*
0.07	49,55,63,72, 83, 90	50,55,62, 70,73,85, 91*	45,60,70,80,8 5,90*

UV – VISIBLE ANALYSIS







UV-VISIBLE SPECTRA RESULTS

a)PDLC doped with MWCNT

Sr.No	%Conc of MWCNT	Wavelength (nm)	% max Absorption
1	0.01	250	0.45
2	0.03	275	0.49
3	0.05	300	0.85
4	0.07	300	1

a)PDLC doped with ZnO.

Sr. No	% Conc. Of ZnO	Wavelength(nm)	% max Absorption
1	0.2	375	0.27
2	0.5	375	0.125
3	0.8	375	0.7
4	1	375	0.45

c)PDLC doped with Fe_2O_3 γ

Sr. No	% Conc. Of Fe_2O_3 γ	Wavelength(nm)	% max Absorption
1	0.01	425	0.825
2	0.03	425	0.825
3	0.05	425	0.825
4	0.07	425	0.825

FTIR SPECTRA RESULTS

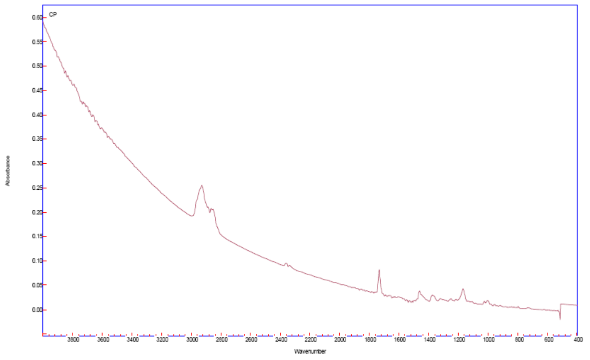
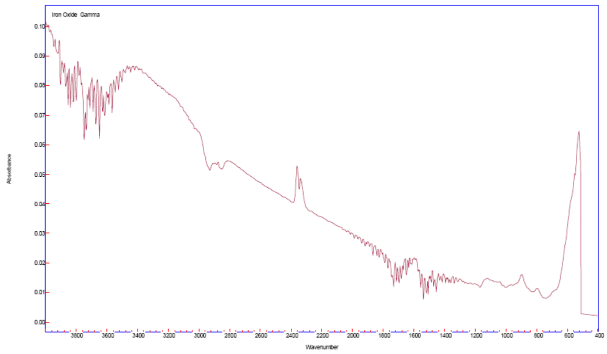
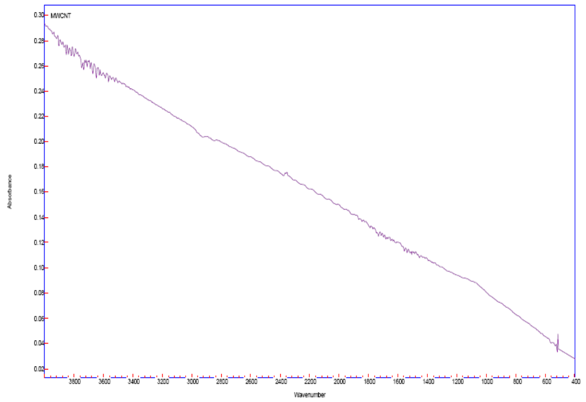
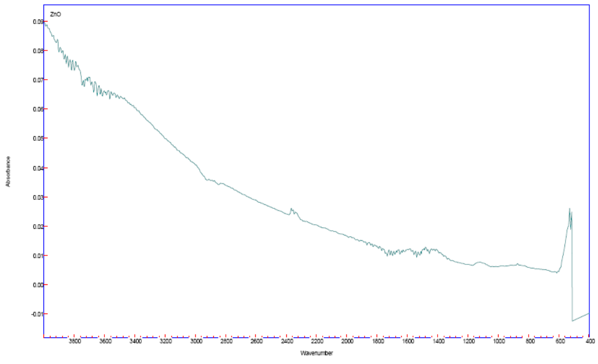
FTIR spectra of PMMA and Cholesteryl Pelargonate reveal strong absorption peaks at the following wave number.

Wave number cm^{-1}	Functional Group	Molecular Motion
1200	Alcohols	O-H(H-bonded), usually broad C-O
1750	Ester	C=O Stretch
2400	Carboxylic acids	O-H stretch
3100	Unsaturated alkenes	=CH stretch
3300	Alcohols	O-H streatch
2950	Alkenes	C-H streatch

Discussion of the Results obtained:

1) Doping nanoparticles transform the LC-polymer system to LC-P_m where P_m is the modified polymer. The properties of modified polymers essentially differ from the properties of pure polymers. These properties mainly depend on the type of material, size and aggregation rate of the particles. Embedded nanoparticles thus modify the optical uniformity, the

electrical conductivity and the clearing point temperatures of the composite sample.

1	CP
	
2	IRON
	
3	MWCNT
	
4	PMMA
	
5	ZNO
	

3) The response so obtained of PDLC doped with MWCNT can be explained by a preliminary partial orientation of LC molecules in the presence of carbon nanotubes in the dispersed Liquid crystal droplets. The orientating action of MWCNT is related to their large dipole moments. [10] The LC molecule seemingly anchors on the CNT walls via π-stacking interaction which alters the binding energy required to overcome the CNT-LC bonding. The variation caused in Clearing Point of the system is a result of the bonding , which may be either from the side walls or head part of LC molecule.

The angular diameter of the rings measured using FPSS at certain phase transition temperatures(PTTs) changed so frequently that the circular ring pattern became unstable over a range .

FTIR spectra of PMMA and Cholesteryl Pelargonate reveal strong absorption peaks at the following wave number.

Wave number cm^{-1}	Functional Group	Molecular Motion
1200	Alcohols	O-H(H-bonded), usually broad C-O
1750	ester	C=O Stretch
2400	Carboxylic acids	O-H stretch
3100	Unsaturated alkenes	=CH stretch
3300	alcohols	O-H streatch
2950	alkenes	C-H streatch

CONCLUSIONS

PDLC+MWCNT

1) Clearing point temperature fluctuating with increase in % concentration of MWCNT. 2) For different concentrations of MWCNT the analysis of the UV-Visible spectra suggest that: a) The central minima shift towards the lower wavelength (i.e.210nm to 190nm) b) The % absorption at the central minima is 30% for 210 nm and 60% for 190nm.

c) The100 % absorption at the central max is observed for 290 nm with 0.07% MWCNT which indicates this proportion is use full in managing the energy band gaps in semiconducting devices. d) it is observed that central max absorption is same for all the proportions of MWCNT The response obtained for PDLC+MWCNT can be explained by a preliminary partial orientation of LC molecules in the presence of carbon nanotubes. The orientating action of MWCNT is related to their large dipole moments. The pure cp exhibiting the SmA* fanshaped texture, phase boundaries are clearly visible, allowing observation of the TGBA* phase even for a narrow temperature interval was disappeared completely *when dopped with MWCNT*

PDLC+ZnO

1) Clearing point temperature increases with increase in % concentration of ZnO. 2) For different concentrations of ZnO Nanoparticles, the analysis of the UV-Visible spectra suggests that: a) The central minima shift towards the lower wavelength (i.e.270nm to 250nm) b) The % absorption at the central minima is 0% for 270 nm and 40% for 250nm.

c) It is observed that a sharp peak is observed is 0.28% for 240nm with 0.5% ZnO which indicates this proportion is use full in managing the energy band gaps in semiconducting devices.

e) The pure cp exhibiting the SmA* fanshaped texture, phase boundaries are clearly visible, allowing observation of the TGBA* phase even for a narrow temperature interval ; was disappeared *when dopped with ZnO*

PDLC+ Fe_2O_3 γ

1) Clearing point temperature fluctuating with increase in % concentration of Fe_2O_3 **γ** 2) For different concentrations of Fe_2O_3 **γ** Nanoparticles the analysis of the UV-Visible spectra suggests that:

a) The central minima occurs at the wavelength of 205nm for all concentrations of Fe_2O_3 **γ**. b) The % absorption at the central minima is 50% for 205 nm. c) It is observed that the central maxima and minima is approximately same for all the proportions with Fe_2O_3 **γ**

3) The pure cp exhibiting the SmA* fanshaped texture, phase boundaries are clearly visible, allowing observation of the TGBA* phase even for a narrow temperature interval; was disappeared completely when dopped with Fe_2O_3 γ 4) Periodic Stripe like textures are observed when dopped with Fe_2O_3 γ

Future projects

Response studies of Nano particle , nanotubes doped liquid crystals can be employed in the solar cells.

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.

4.4 *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.

3.6 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

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REFERENCES

[1]Chandrashekhar, liquidCrystals,2ndEdition",Cambridge University Press,Cambridge,London(1992)

[2] Demus D Diele S,Grande S and Sackmann H.Z, "Advances in liquid cryatals",6,edited by G.H Brown(London Academic),1(1983)

[3] Fowles Grant R, "Introduction to Modern Optics", Second Edition, Dover Publications, New York(1989)

[4] Gupta Sureshchandra J, "Indian J of Pure Appl Phys",37 620 (1999)

[5] Gupta Sureshchandra J, "J of Optics",29 pp 53-62(2000)

[6]GuptaSureshchandr.J,"Liquid Crystals: Chemistry, Physics and Applications,"Proceedings of SPIE,Poland),44147 23 (2000).

[7] Gupta S J,Gharde R A and Tripathi A R,"Molecular Crystals & Liquid Crystals",(Procs. Of ILCC2000,Japan) 364 461 (2000).

[8] Peter J Collings and Michael Hird ,"Introduction to Liquid crystals (Chemistry and Physics)",Taylor & Francis Publishers Ltd,London(1997)

[9] Peter. J.Collings, Jay S.Patel, "Handbook of Liquid Crystal Research".

[10] Satyen Kumar, "Liquid Crystals: Experimental Study of Physical Properties and Phase Transitions", Cambridge University press.