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Synthesis and Investigation of Liquid Crystalline Property of a New Thermotropic Liquid Crystalline System with Terminal Chloro Group and DSC study

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ABSTRACT
A novel azoester series with chloro terminal group was synthesized and characterized for mesomorphic properties. It consists of 12 azoester derivatives from esterification reaction between 4-n-alkoxy-3-methoxy cinnamic acid and 4-hydroxy-2-methyl phenyl azo-4-chloro benzene. The isotropic temperature of homologous series LC compounds decreased with the increased of carbon in flexible chain. The present series is fully nematogenic and partially smectogenic in nature. The mesophase length is minimum 3.8 ^{0}C to maximum 64.3^{0}C.Mesophase property commences from first homologue of novel azoester series. Some mesogenic LC compounds were characterized by fourier-tranform infrared spectroscopy (FT-IR), Mass spectroscopy, proton nuclear magnetic resonance (^{1}H-NMR) and elemental analysis. The mesogenic phases of novel azoester LC compounds confirm by polarized optical microscopy (POM) and their thermal properties of some homologue characterized by differential scanning calorimeter. Mesomorphic behaviours of novel azoester series are compared with structurally similar series.

Key Word: *Smectogenic, Nematogenic, Mesophase, DSC, Azoester*

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I. INTRODUCTION

The intermediate state between a crystalline solid and liquid is known as a liquid crystal compound (LC). The LC compounds have some typical properties of liquid and crystal. The LC compounds have special types of shape. The research cover many area of science such as biomedical carriers, nanomaterial, display devices, light emitting diodes, semiconductor materials, coloring agent, etc.[1-5] As a novel liquid crystal compound have special types of properties like as a lower crytallinity and good solubility as well as middle range melting point. Typical compound shows liquid crystalline properties with terminal electronegative polar group as a Cl, F, Br and I. The Chloro group provided molecular polarizability, thus related with intramolecular interaction, hence molecular shows polymorphic [6].The liquid crystalline compound classified in two types: thermotropic liquid crystal and lytropic liquid crystal base on orientation of molecular. The thermotropic LC compound most study in research. The thermotropic liquid crystal further classified in two types: Smectic(Sm) and Nematic (N) base on arrangement of molecular after heating on POM [7-9].

II EXPERIMENTAL PROCEDURES

2.1 Material

4-Hydroxy-3-methoxy benzaldehyde, n-alkyl bromides($C_nH_{2n+1}Br$), K_2CO_3, Malonic Acid, dicyclohexylcarbodiimide(DCC), 4-dimethylamino pyridine(DMAP), 4-chloro aniline, m-cresol, Sodium Nitrite, Sodium hydroxide, pyridine, piperidine and other solvent used in synthesis were obtain from commercial available from Spectrochem, Merck and Sigma –Aldrich. Purity of all these compounds was check by TLC.

2.2 Synthesis of 4-n-Alkoxy-3-methoxy cinnamic acid[Int-A]

3-Methoxy-4-n-alkoxy cinnamic acid were synthesized by refluxing 4-hydroxy-3-methoxy aldehyde (1 equiv.) with corresponding n-alkyl bromides (1.5 equiv.) in the presence of potassium carbonate (1.2 equiv.) and DMF solvent[10].The reaction monitoring by TLC. After completion of reaction the reaction mixture pore in ice cold water, solid 3-methoxy-4-n-alkoxy cinnamic acid product fall out. The precipitate filtered by help of vacuum filtrationand drying to obtain crude product. The crude product recrystallised in ethanol to further use. The resulting product 4-n-Alkoxy-3-methoxy benzaldehyde (1 equiv.) were reacted with malonic acid (1.2 equiv.) in the presence of 1-2 drops of piperidine and pyridine as solvent[11].The reaction completion is check out by TLC. After completion of reaction mixture was pore in cold acidic water (H_2O: HCl). The solid product filtered by vacuum filtration and obtain crude product is recrystallised in ethanol for further used.

2.3 Synthesis of 4-((4-Chlorophenyl)diazenyl)-3-methyl phenol[Int-B]

4-Chloro aniline (1 equiv.) was weighed in a 500 mL beaker and adds mixture of HCl and water. The mixture was stirred using magnetic stirrer in ice bath until solid dissolved. A appropriate amount of $NaNO_2$ was dissolved in water and add in reaction slowly with precaution. Now reaction mixture put stirring for 1 hour.In other hand phenol (1 equiv.) and NaOHwere dissolved in appropriate water. After cooling reaction mixture mixed both solution slowly with precaution and was stirred for more than 1 hour at the end of reaction yellow color precipitate are fall out[12]. This mixture filtered out by used of vacuum filtration and crude product further used after recrystallised in ethanol. The reaction yield is 79.3%.

2.4 Synthesis of 4-(4’-n-Alkoxy-3’-methoxy cinnamoyloxy) 3-methyl azo 4”-chloro benzene

The 4-n-Alkoxy-3-methoxycinnamic acid(Int-A) (1 equiv.) dissolving in appropriate dichloromethylene solvent in 250 mL single neck RBF. Then add DCC (1.2 equiv.) and pinch of DMAP. Put reaction mixture for stirring for 1 hour at room temperature. Then add 4-((4-Chlorophenyl)diazenyl)-3-methyl phenol[Int-B] (1 equiv.)and the solution was stirred for 24 hour at room temperature [13]. The reaction monitoring by TLC . After completion of reaction the solution was filtered in vacuum filtration and remove DCU precipitate with care full and solvent was removed by evaporation using rotary evaporator. The crude product recrystallized in ethanol. The yield of percentage of all homologue recorded in table1.

Scheme 1: Synthesis Route of novel azoester series PCOCCA-n

III. CHARACTERIZATION

Some member of series was characterized by elemental analysis on EuroEA Elemental Analyzer. IR Spectra were recorded on Shimadzu FTIR-8400, ^{1}H NMR were recorded on Bruker spectrometer using $CDCl_3$ solvent, Mass spectra were recorded on Shimadzu GC-MS Model No. QP-2010. The thermal behaviour recorded on Differential scanning calorimeter model no.Shimadzu,shinapore DSC-60 10.8. and mesomorphic properties recorder on polarized optical microscopy model no.Nikon Eclipse 400/TU Plan ELWD 20 X/0.40.

3.1 ANALYTICAL DATA

3.1.1.Elemental analysis

Table 1: Elemental analysis of present homologous series PCOCCA-n

No	Compound Code	Molecular Formula	% Theoretical (%Found)		
			C	H	N
1	PCOCCA-3	$C_{26}H_{25}ClN_2O_4$	67.17(67.22)	5.42(5.48)	13.76(13.79)
2	PCOCCA-4	$C_{27}H_{27}ClN_2O_4$	67.71(67.75)	5.68(5.65)	13.36(13.42)
3	PCOCCA-6	$C_{29}H_{31}ClN_2O_4$	68.70(68.65)	6.16(6.19)	12.62(12.69)
4	PCOCCA-7	$C_{30}H_{33}ClN_2O_4$	69.15(69.09)	6.38(6.43)	12.28(12.35)

3.1.2.Spectral data

^{1}H NMR in *ppm* spectra of methyloxy derivative (PCOCCA-1): ^{1}H NMR in δ ppm 400 MHz, 2.77(s,3H, -Ar($\underline{CH_3}$)-N=N-Ar) 3.96-3.97(d,6H, -Ar($\underline{OCH_3}$)-CH=CH-) 6.51-6.55(d,1H, -$\underline{CH}$=CH-COO-) 6.92-6.94(d,1H, -$\underline{Ar}$-CH=CH-) 7.09-7.12(m,1H, -$\underline{Ar}$-CH=CH-) 7.14-7.15(d,1H, -$\underline{Ar}$-CH=CH-) 7.20-7.22(t, 2H –$\underline{Ar}$-Cl) 7.49-7.51(t, 2H, -$\underline{Ar}$-N=N- Ar) 7.74-7.76(d, 1H, -$\underline{Ar}$-N=N-Ar) 7.84(s,1H, -CH=$\underline{CH}$-COO-) 7.87-7.89(m,2H, -N=N-$\underline{Ar}$-Cl) NMR data is reliable with the molecular structure.

^{1}H NMR in *ppm* spectra of octyloxy derivative (PCOCCA-8): ^{1}H NMR in δ ppm 400 MHz, 0.89-0.93(t,3H, -O-$(CH_2)_7$-$\underline{CH_3}$) 1.31(s, broad peak, 6H, -$(\underline{CH_2})_3$- CH_3) 1.49(s, 3H, -Ar(m-$\underline{CH_3}$)-N=N-Ar) 1.47-1.56(m, 2H, -$\underline{CH_2}$–$(CH_2)_3$ -CH_3) 1.86-1.93 (m, 2H, - $\underline{CH_2}$–$(CH_2)_4$ - CH_3) 2.76(s,2H,-$\underline{CH_2}$–CH_2–O-Ar) 3.49 (s,2H, -Ar-$\underline{OCH_3}$)

4.07-4.11 (t,2H, -Ar-<u>OCH$_2$</u>-) 6.49-6.53(d,1H, -<u>CH</u>=CH-COO-) 6.91-6.93(d,1H, -<u>Ar</u>-CH=CH-) 7.09-7.12(m,1H, -<u>Ar</u>-CH=CH-) 7.141-7.149(d,1H, -<u>Ar</u>-CH=CH-) 7.17-7.20(m, 2H,-<u>Ar</u>-Cl) 7.49-7.52(m,2H, -<u>Ar</u>-N=N-Ar-) 7.73-7.76(d, 1H, -<u>Ar</u>-N=N-Ar) 7.83(s,1H,, -CH=<u>CH</u>-COO-) 7.87-7.89 (t,2H, -N=N-<u>Ar</u>-Cl)The NMR data is reliable with the molecular structure.

Mass spectra of propyloxy derivative (PCOCCA-3);m/z (relative intensity %): 464 (M$^+$)(5%), 219 (100%-ester linkage break), 245(5%- ester linkage break) .The mass data is reliable with the molecular structure.

Mass spectra of heptyloxy derivative (PCOCCA-7):m/z (relative intensity %): 520 (M$^+$)(5%), 275 (100%-ester linkage break), 245 (5%- ester linkage break) .The mass data is reliable with the molecular structure.

IR spectra in *cm* $^{-1}$of ethyloxy derivative (PCOCCA-2): (KBr) 3054.35 (C-H stretching of alkene disubstituted), 2978.48 & 2839.31 (C-H Strerching of –(CH$_2$)- group of alkyl chain), 1728.28 (C=O stretching of carbonyl carbon of ester), 1589.40 (C=C stretching of alkene), 1519.96 & 1473.66 (C=C stretching of aromatic ring), 1411.94 (-N=N- diazo), 1134.18 (C-O stretching of ester group), 833.28 (para disubstiuted benzene ring). The IR data is reliable with the molecular structure.

IR spectra in *cm* $^{-1}$of butyloxy derivative (PCOCCA-4):(KBr) 3067.06 (C-H stretching of alkene disubstituted), 2947.33 & 2839.31 (C-H Strerching of –(CH$_2$)- group of alkyl chain), 1735.99 (C=O stretching of carbonyl carbon of ester), 1589.40 (C=C stretching of alkene), 1524.24 & 1465.95 (C=C stretching of aromatic ring), 1419.66 (-N=N- diazo), 1126.47(C-O stretching of ester group), 833.28(para disubstiuted benzene ring). The IR data is reliable with the molecular structure.

3.1.3.Representative spectra of synthesized compound

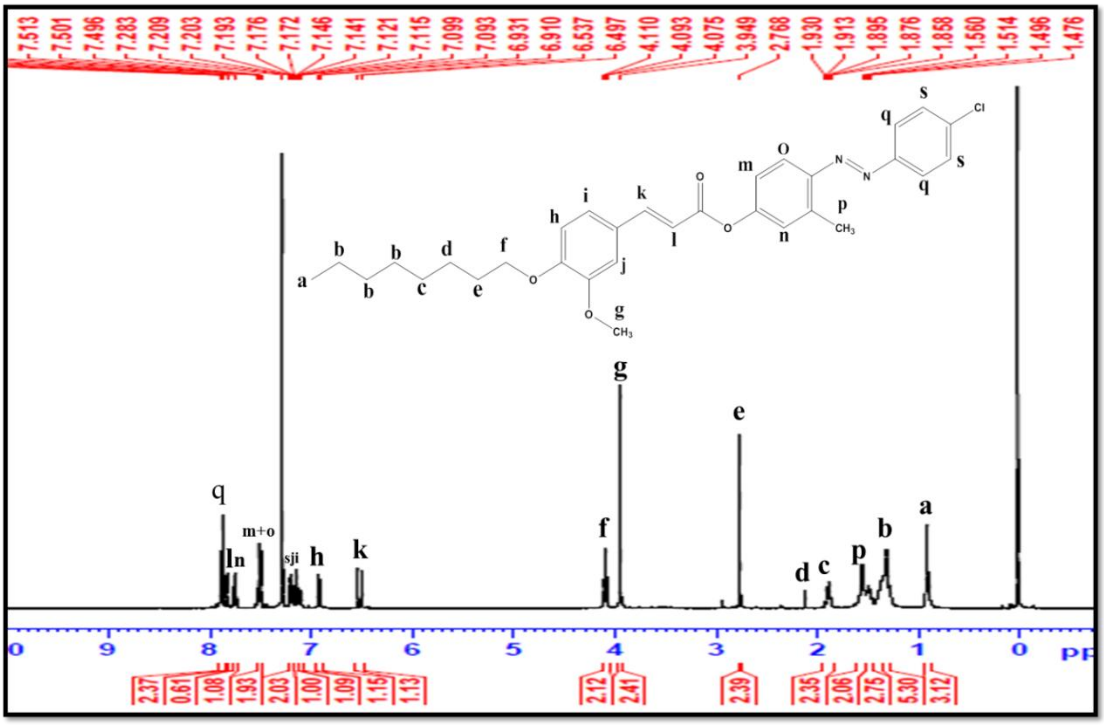

Figure 1:^{1}H-NMR of Octyloxy derivative(PCOCCA-8)

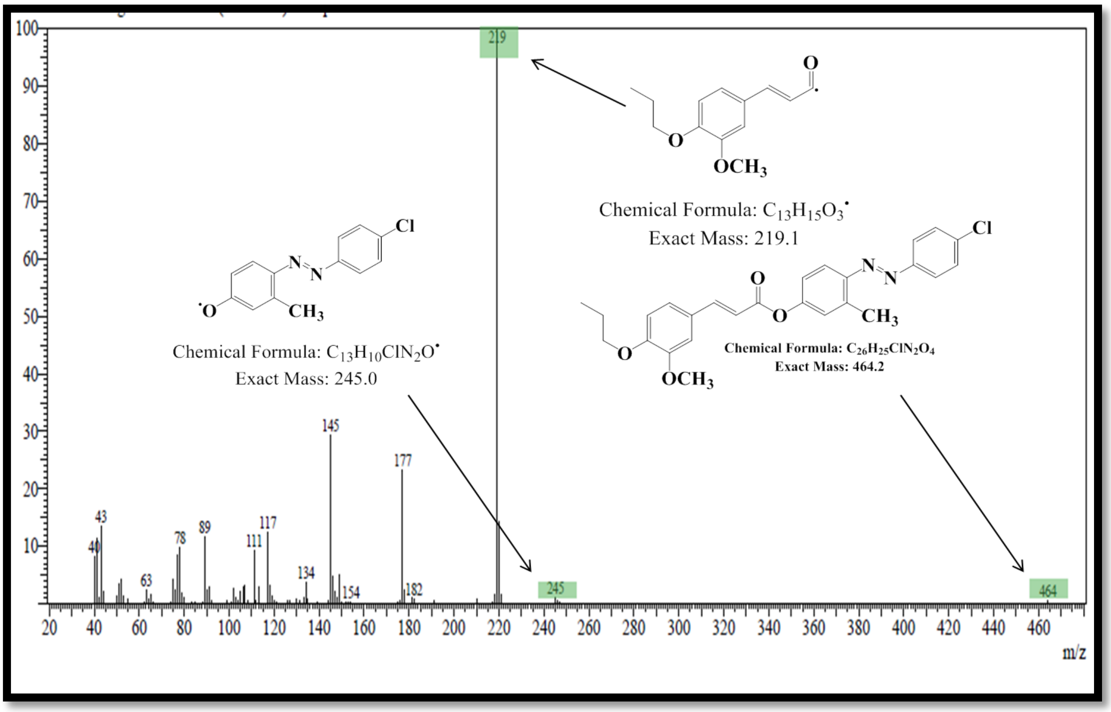

Figure 2: Mass spectra of propyloxy derivative(PCOCCA-3)

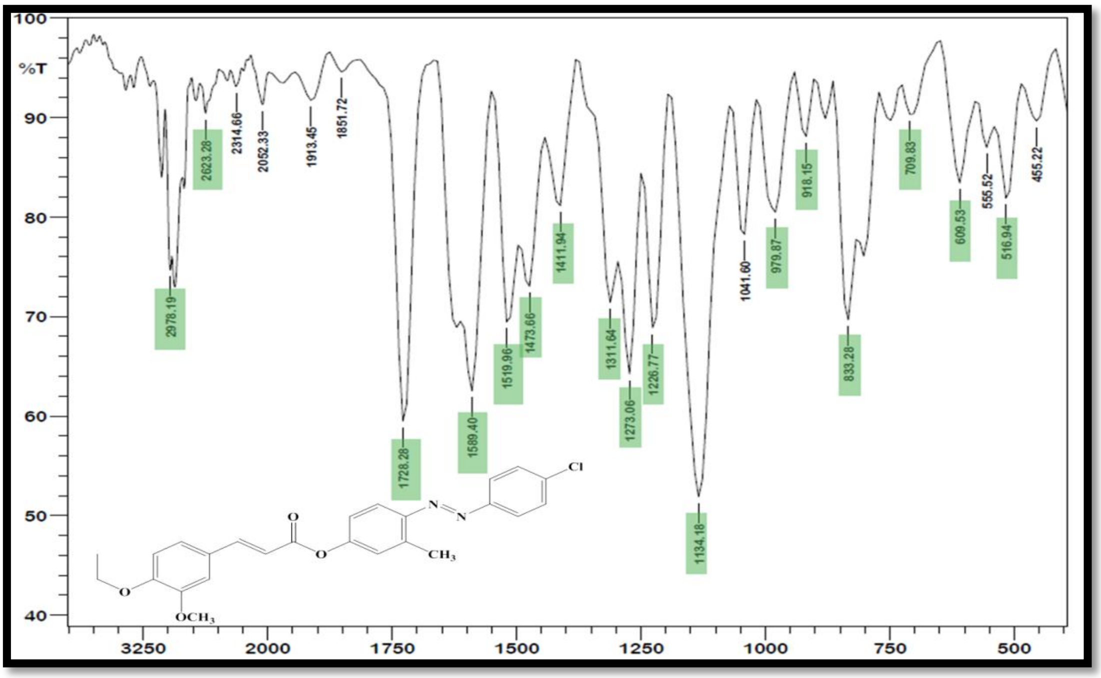

Figure 3:IR Spectra of ethyloxy derivative (PCOCCA-2)

IV. RESULT AND DISCUSSION

The novel homologous series of 4-(4’-n-Alkoxy-3’-methoxy cinnamoyloxy) 2-methyl phenyl azo 4’’-chloro benzene ,were synthesize by esterification reaction between 4-n-Alkoxy-3-methoxy cinnamic acid [Int-A] and 4-((4-Chlorophenyl)diazenyl)-3-methylphenol [Int-B].The intermediate 4-n-Alkoxy-3-methoxy cinnamic acid [Int-A] and 4-((4-Chlorophenyl)diazenyl)-3-methylphenol [Int-B] is non-liquid crystalline in nature but both combine to each other than form liquid crystalline nature. The methodical study of homologous series have allowed to understanding of co-relation between molecular structure and liquid crystal behaviour. The twelve compound synthesized and their phase transition temperature was recorded in polarizing optical microscope Nikon Eclipse 400/TU Plan ELWD 20X/0.40. The present investigated series are partially smectogenic and fully nematogenic in nature.

Table 2:Phase transition temperature of series PCOCCA-n in ^{0}C

Compound	No.of carbon in alkyl chain (C_nH_{2n+1})	Transition Temperature in °C		
		Sm	**N**	**Isotropic**
PCOCCA-1	Methyl	-	172.4	176.2
PCOCCA-2	Ethyl	98.4	156.5	162.7
PCOCCA-3	Propyl	-	150.4	160.2
PCOCCA-4	Butyl	-	118.8	159.8
PCOCCA-5	Pentyl	-	139.8	149.9
PCOCCA-6	Hexyl	-	120.4	144.4
PCOCCA-7	Heptyl	-	110.4	125.8
PCOCCA-8	Octyl	-	97.4	122.9
PCOCCA-10	Decyl	-	113.2	121.6
PCOCCA-12	Dodecyl	-	102.7	117.7
PCOCCA-14	Tetradecyl	107.3	116.0	121.3
PCOCCA-16	Hexadecyl	78.7	100.3	110.3
(Sm)-Smectic,(N)-Nematic				

According to transition temperature graph of LC phase behaviour were plotted transition temperature in ^{0}C Vs number of carbon in flexible alkyl chain shown in figure 4.

The Cr-Sm/N transition curve denoted by dotted line **(⋯⋯●⋯⋯).** The odd-even effect observed for PCOCCA-1 to PCOCCA-6 compounds, then disappears odd-even effect from PCOCCA-6 to PCOCCA-8 compound. The transition temperature for Cr-Sm/N curve,it continues decrease with increased with number of carbon in flexible n-alkyl chain on left end of corresponding molecules for PCOCCA-5 to PCOCCA-8.The further odd-even effect observed between PCOCCA-7 and PCOCCA-16 homologues. It is interesting notice that the odd-even effect and decreasing manner are alternating to each other for Cr-Sm/N transition. The Sm-N transition curve denoted by continue line (−▲−), it shows decreasing manner graph pattern observed for PCOCCA-14 to PCOCCA-16 compound. The N-I transition curve denoted by continue line (−■−),it continues decrease with increased number of carbon in n-alkyl chain except PCOCCA-14 homologue.

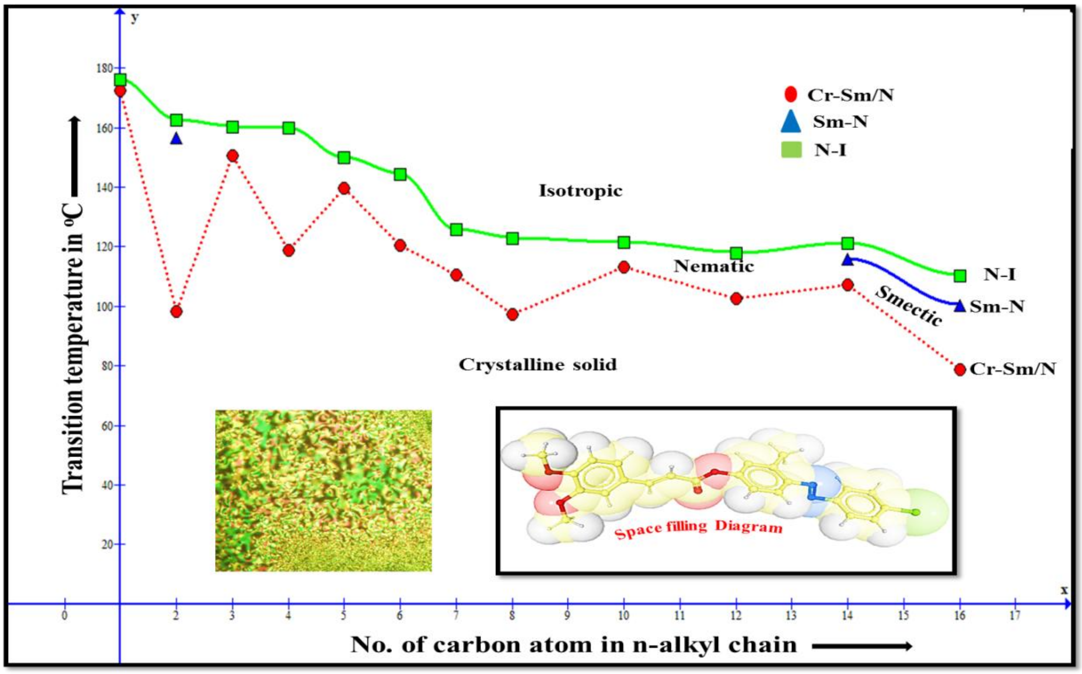

Figure 4:Phase behaviour of series PCOCCA-n

The N-I transition temperature of PCOCCA-7, PCOCCA-8, PCOCCA-10, PCOCCA-12 and PCOCCA-14 almost equal to each other, so N-I transition graph is slightly linear between PCOCCA-7 to PCOCCA-14 homologues. The transition temperature of some compound of present investigated series also confirm by DSC thermal analysis. From table 2, the all compound consist middle range melting point. The smectic transition temperature of present series is very low.

The present investigated series in which compound PCOCCA-1 to PCOCCA-16 consist nematogenic mesophase and compound PCOCCA-14 to PCOCCA-16 consist smectogenic mesophase. According to table 2, all compound of series PCOCCA-n is enatiotropic in nature. The series is fully nematogenic and partially smectogenic in nature. Total twelve compounds in which two compound PCOCCA-14 to PCOCCA-16 are polymesomophic in nature because they have both phase smectic as well as nematic.

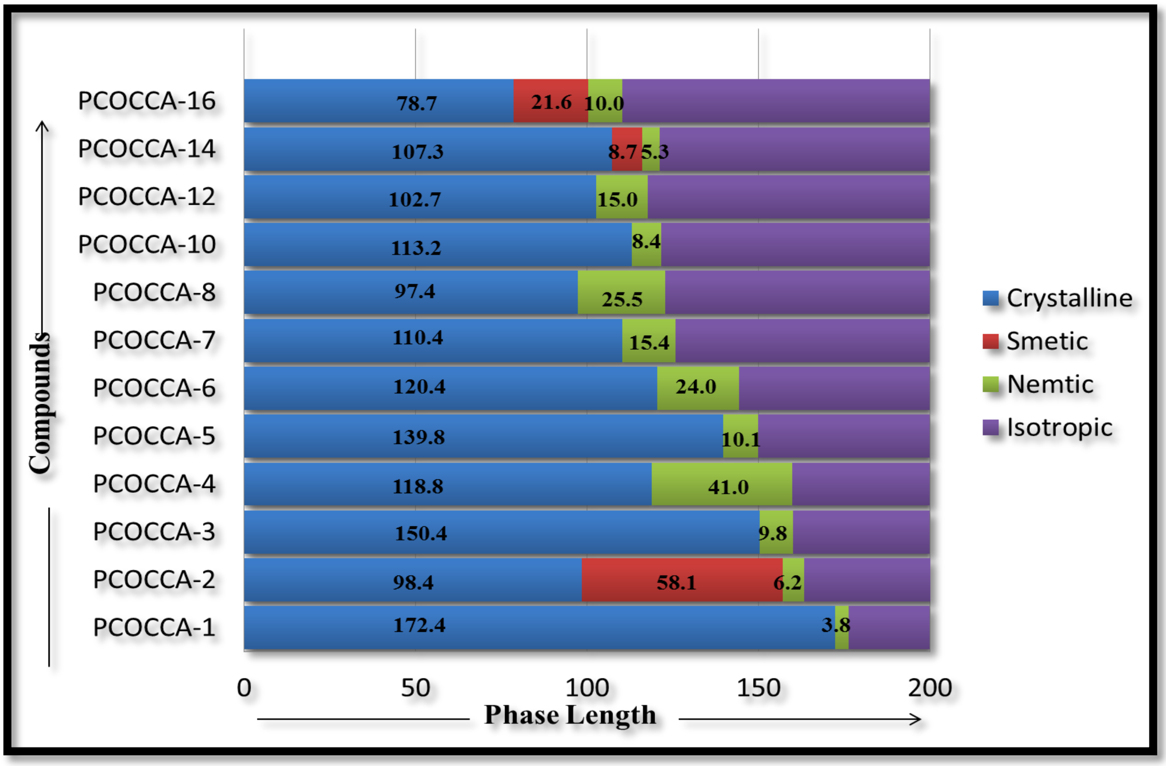

Figure 5:Mesophase lengths diagram of series PCOCCA-n

The figure 5 indicated mesophase lengths of whole compound of series PCOCCA-n. The minimum and maximum mesophase length of smectic and nematic phase of present series is 8.7 ^{0}C to 58.1^{0}C and 3.8^{0}Cto 41.0 ^{0}Crespectively. The values of thermal stability of smectic and nematic phase are 124.2 ^{0}C and 139.4 ^{0}C respectively. The smectic mesophase length of PCOCCA-14 homologue and nematic mesophase length of PCOCCA-10 homologue are almost equal to each other. The nematic mesophase lengths of PCOCCA-5 and PCOCCA-16 homologues are almost equal to each other.

4.1 DSC thermal analysis

The DSC analysis gives satisfactory information about liquid crystal compound. The DSC is useful analytical technique and it supportive analysis of liquid crystalline nature [14-18]. In present work enthalpy of transition of compound PCOCCA-2 to PCOCCA-5, PCOCCA-7 and PCOCCA-10 to PCOCCA-14 were measured by the help of DSC analysis at the temperature rate 10 ^{0}C/min in heating scan. The figure 6 to13 indicates DSC thermogram of compound PCOCCA-2 to PCOCCA-4, PCOCCA-7 and PCOCCA-10 to PCOCCA-14 respectively. Their mesophase length, enthalpy change, transition temperature and entropy change in heating scan is recorded in Table 3. The figure6 is DSC thermogram of PCOCCA-2 compound in which two endothermic sharp peaks are observed at 98.4 ^{0}C and 156.5^{0}C temperature respectively. These endothermic peaks define crystal (Cr) → smectic mesophase and Smectic mesophase →nematic mesophase transition. The figure 7 is DSC thermogram of PCOCCA-3 compound in which one endothermic sharp peak are observed at 150.4 ^{0}C temperature. These endothermic peaks define crystal (Cr) → nematic mesophase transition. The figure 8 is DSC thermogram of PCOCCA-4 compound in which one endothermic sharp peak are observed at 118.8 ^{0}C temperature. These endothermic peaks define crystal (Cr) → nematic mesophase transition. The figure 9 is DSC thermogram of PCOCCA-5 compound in which one endothermic sharp peak are observed at 139.8 ^{0}C temperature. These endothermic peaks define crystal (Cr) → nematic mesophase transition.The figure10 is DSC thermogram of PCOCCA-7 compound in which two endothermic peaks are observed at 110.4 ^{0}C and 125.8^{0}C temperature respectively. These two endothermic peaks define crystal (Cr) → nematic mesophase and nematic mesophase→isotropic (I) phase transition respectively. The figure 11 is DSC thermogram of PCOCCA-10 compound in which one endothermic sharp peak are observed at 113.2 ^{0}C temperature. These endothermic peaks define crystal (Cr) → nematic mesophase transition. The figure 12 is DSC thermogram of PCOCCA-12 compound in which one endothermic sharp peak are observed at 102.7 ^{0}C temperature. These endothermic peaks define crystal (Cr) → nematic mesophase transition.The figure 13 is DSC thermogram of PCOCCA-14 compound in which two endothermic sharp peaks are observed at 107.3 ^{0}C and 116.0 ^{0}C temperature respectively. These endothermic peaks define crystal (Cr) → smectic mesophase and Smectic mesophase →nematic mesophase transition. Here very close temperature change between mesophase transition and isotropic transition, So isotropic peak are not observed in PCOCCA-2, PCOCCA -3, PCOCCA -5, PCOCCA -10, PCOCCA -12 and PCOCCA -14 homologues in temperature rate 10 ^{0}C/min in heating scan.

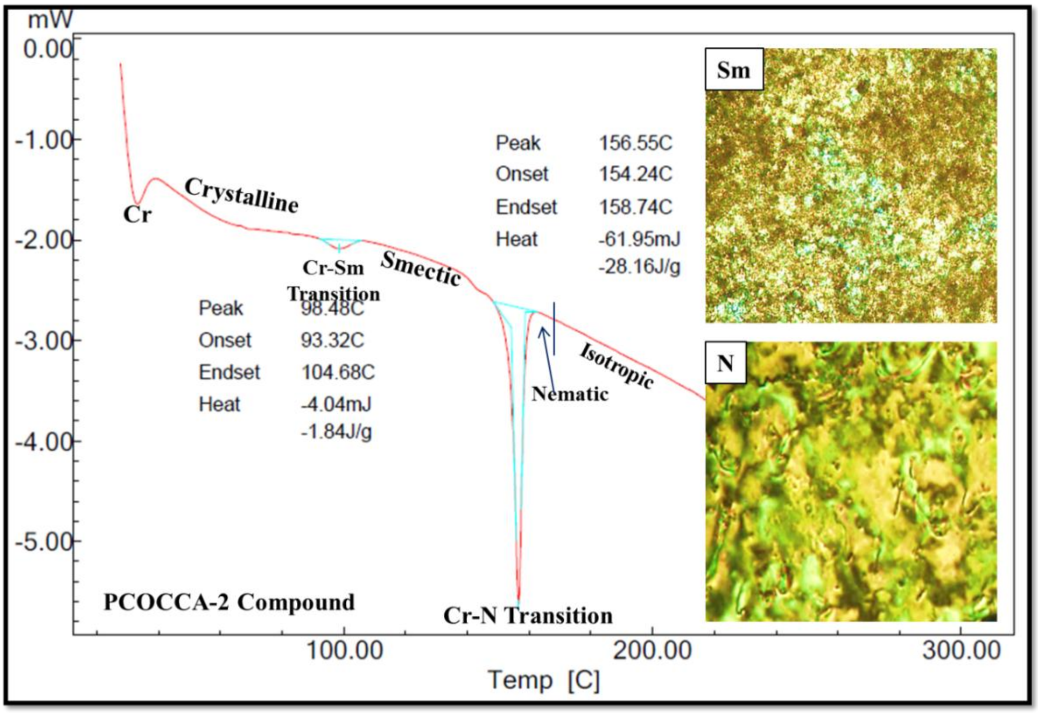

Figure 6: DSC Thermogram of PCOCCA-2 compound

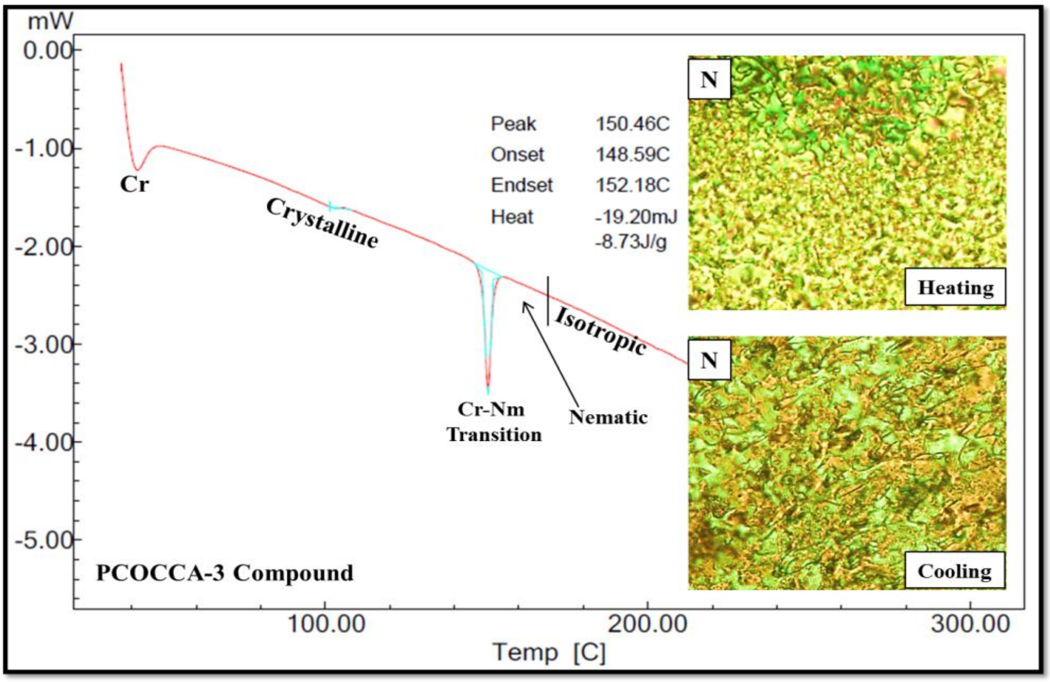

Figure 7: DSC Thermogram of PCOCCA-3 compound

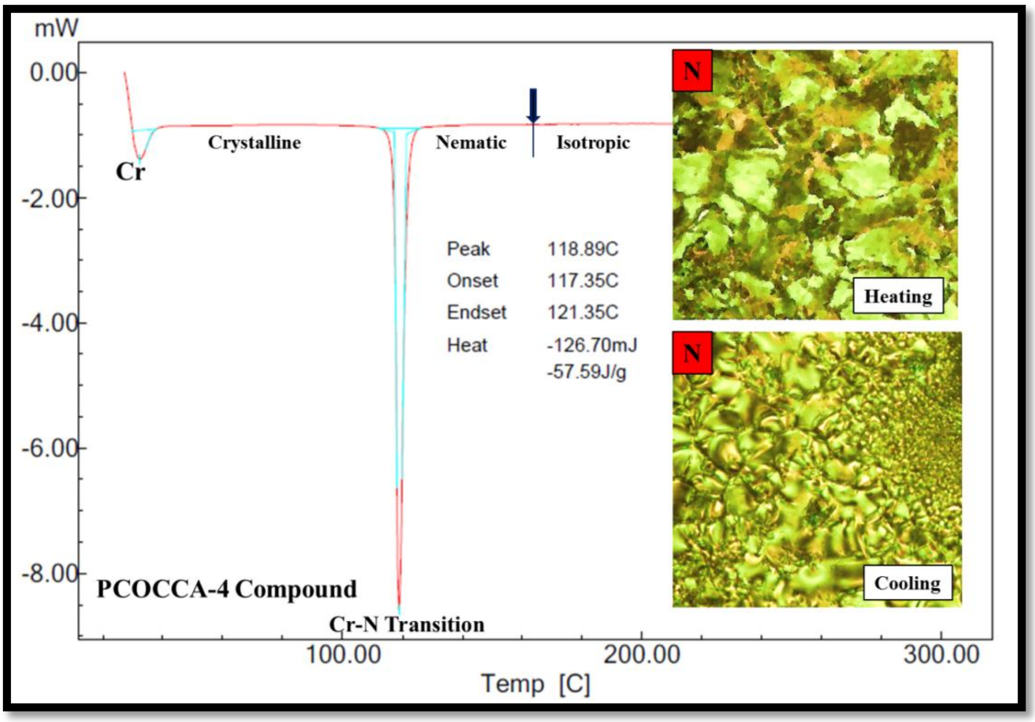

Figure 8:DSC Thermogram of PCOCCA-4 compound

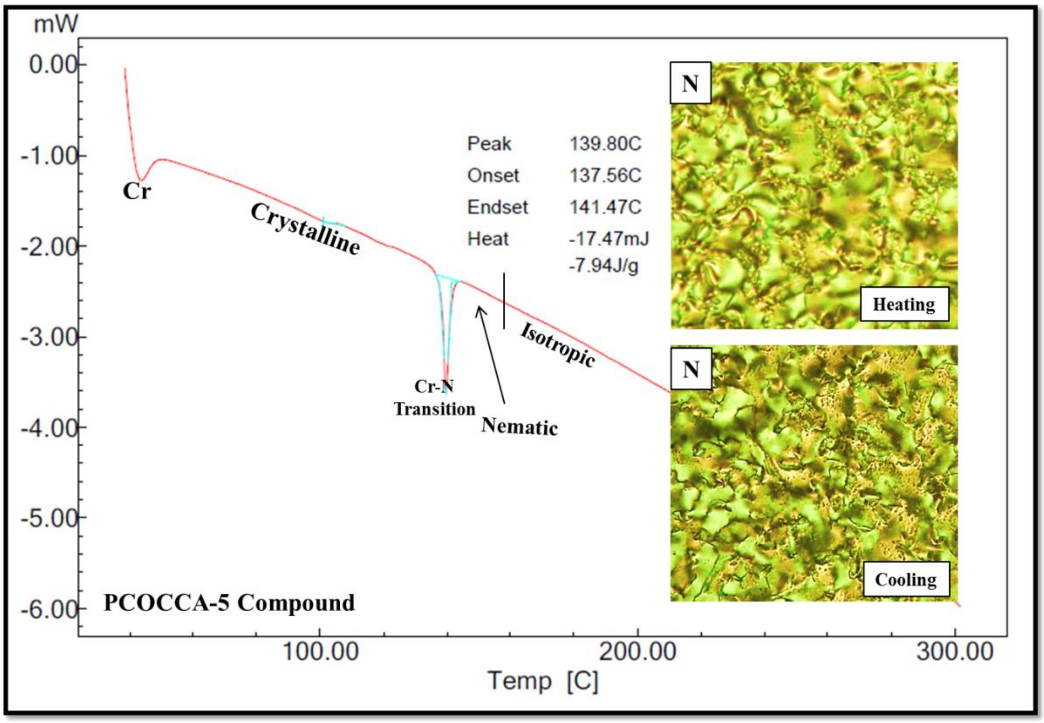

Figure 9: DSC Thermogram of PCOCCA-5 compound

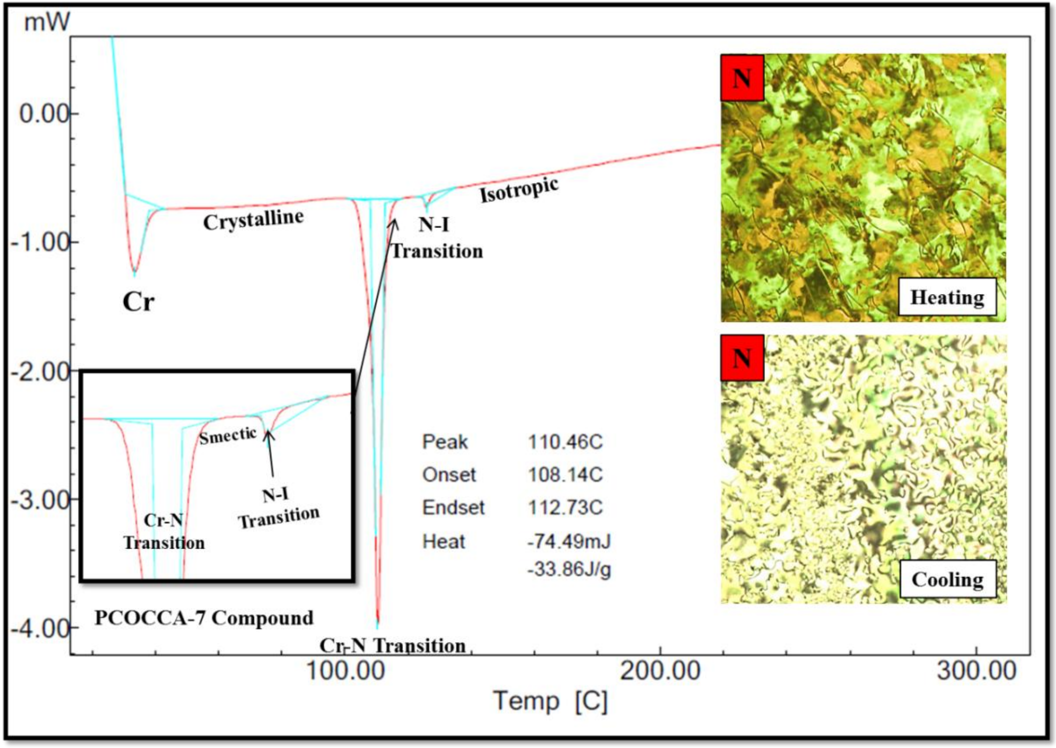

Figure 10: DSC Thermogram of PCOCCA-7 compound

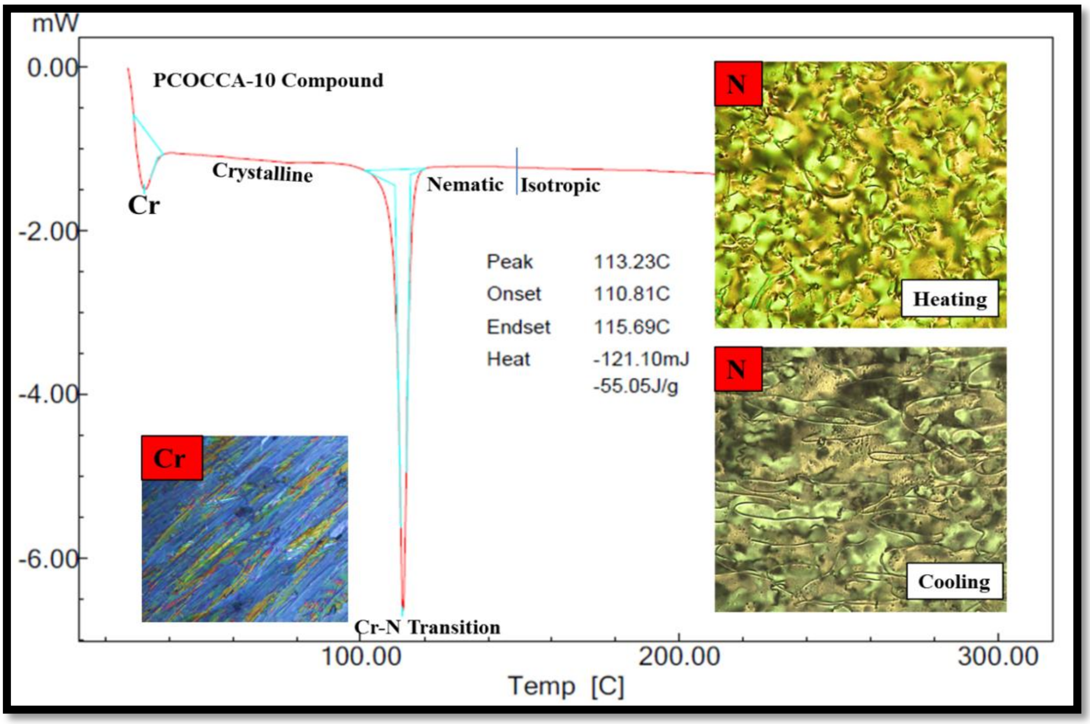

Figure 11: DSC Thermogram of PCOCCA-10 compound

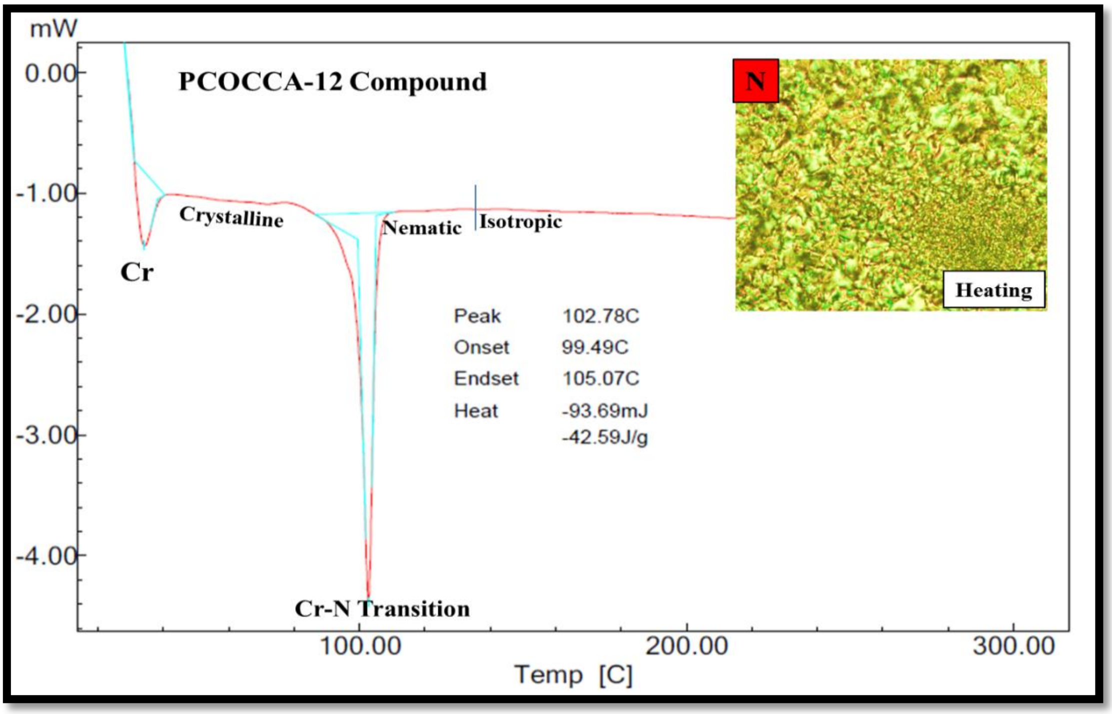

Figure 12: DSC Thermogram of PCOCCA-12 compound

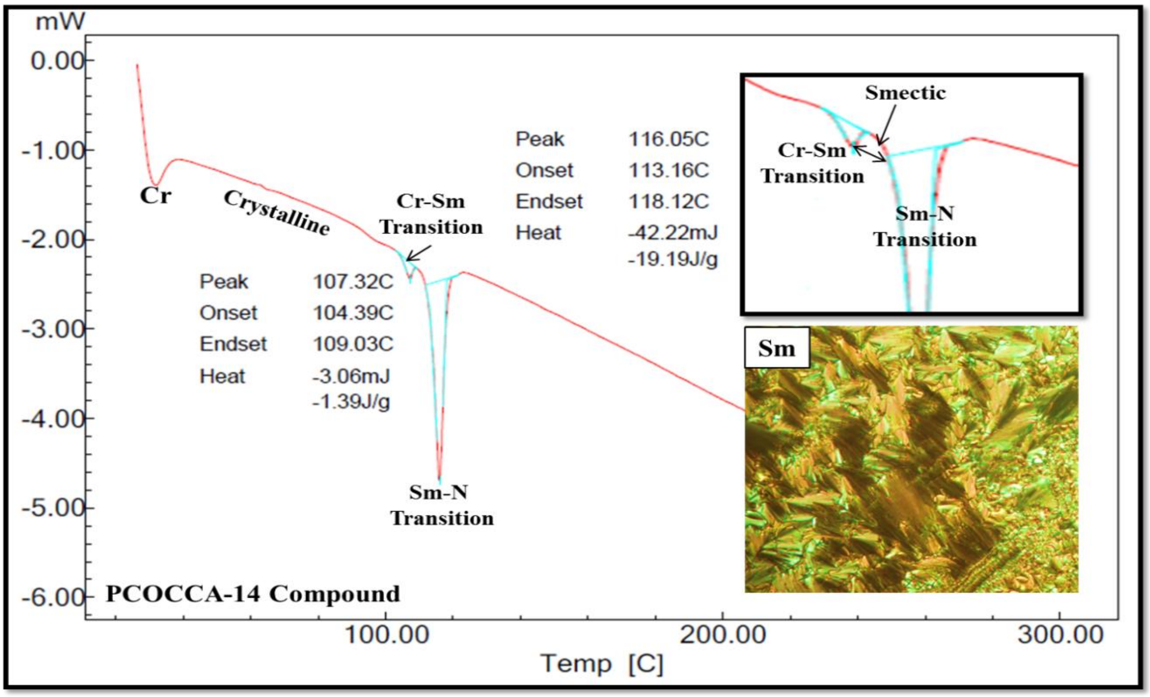

Figure 13: DSC Thermogram of PCOCCA-14 compound

Table 3: Enthalpy, Entropy change and Phase length from DSC thermal analysis

Compound	Transition	Transition Temperature(^{0}C)	ΔH Jg^{-1}	ΔS=ΔH/T Jg^{-1}K^{-1}	Phase length
PCOCCA-2	Cr-Sm	98.4	1.84	0.0049	Sm-58.1
	Sm-N	156.5	28.16	0.0655	N-6.2
PCOCCA-3	Cr-N	150.4	8.73	0.0206	N-9.8
PCOCCA-4	Cr-N	118.8	57.59	0.1469	N-41.0
PCOCCA-5	Cr-N	139.8	7.94	0.0192	N-10.1
PCOCCA-7	Cr-N	110.4	33.86	0.0883	N-15.4
PCOCCA-10	Cr-N	113.2	55.05	0.1425	N-8.4
PCOCCA-12	Cr-N	102.7	42.59	0.1133	N-15.0
PCOCCA-14	Cr-Sm	107.3	1.39	0.0036	Sm-8.7
	Sm-N	116.0	19.19	0.0493	N-5.3

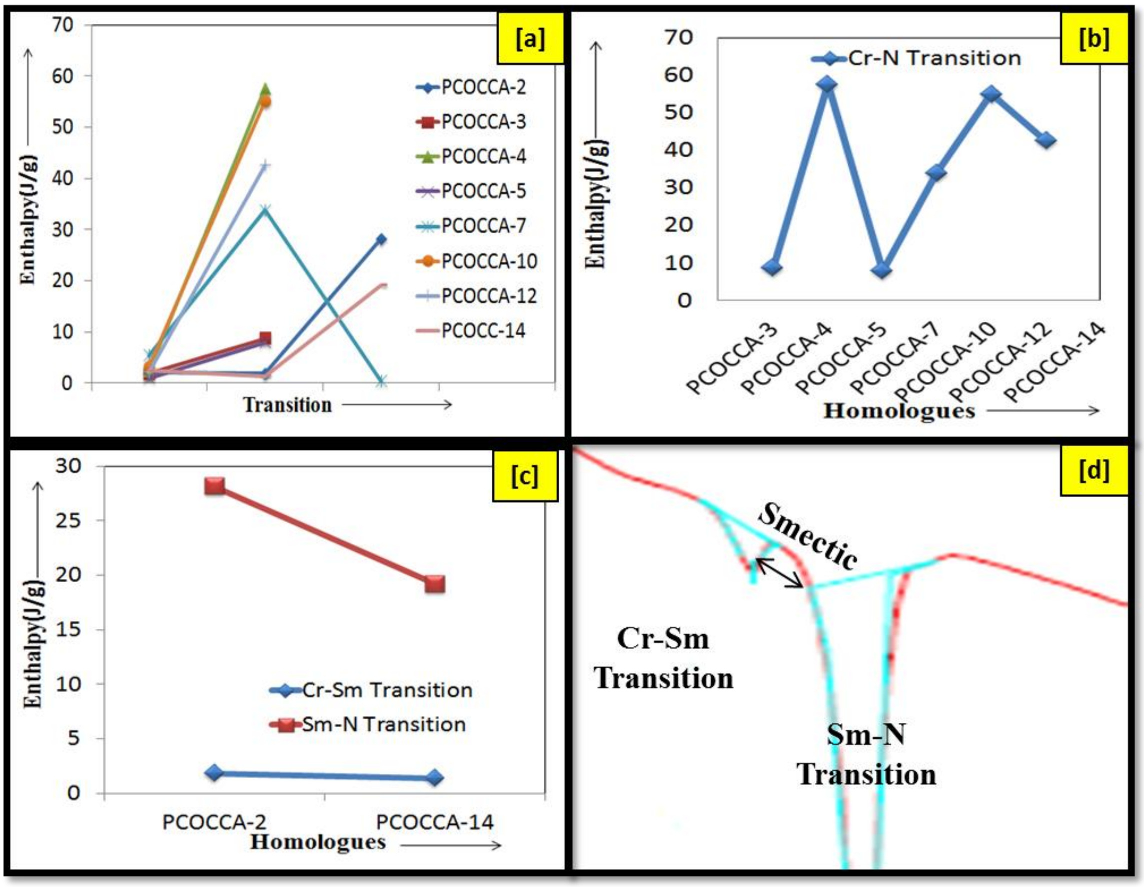

Figure 14:(a) Influence of the alkyl chain on the enthalpy of the PCOCCA-n during hating scan on DSC of PCOCCA-2 to PCOCCA -5, PCOCCA -7, PCOCCA -10 and PCOCCA -12 homologues, (b) Influence of Cr-N transition enthalpy of PCOCCA -3 to PCOCCA -5, PCOCCA -7 , PCOCCA -10 and PCOCCA -12 homologues, (c) Influence of Cr-Sm transition enthalpy and Influence of Sm-N transition enthalpy of PCOCCA -2 and PCOCCA -14 homologues and (d) Close transition observed in PCOCCA -14 homologue

The phase transition enthalpy of PCOCCA-2 to PCOCCA -5, PCOCCA -7, PCOCCA -10 and PCOCCA -12 homologues for heating cycle from DSC analysis based on their influence with addition of methylene group mention in figure 14(a). From figure 14(b) clearly observed that enthalpy change (∆H) of Cr-N transition for PCOCCA -3 to PCOCCA -5, PCOCCA -7, PCOCCA -10 and PCOCCA -12 homologues shows zig-zag pattern. From figure 14(c) clearly observed that enthalpy change (∆H) of Cr-Sm transition for PCOCCA -2 and PCOCCA -14 homologues shows linear manner graph and enthalpy change (∆H) of Sm-N transition for PCOCCA -2 and PCOCCA -14 homologues shows descending manner graph. The close transition observed between Cr-Sm and Sm-N for PCOCCA -14 homologue is mention in figure 14(d).From table 3 the value of entropy changes for Cr-N transition of PCOCCA -4 and PCOCCA -10 equal to each other. According DSC analysis proves that mesophase length of PCOCCA -7 and PCOCCA -12 compounds is equal to each other.

4.2 POM texture study

The POM study of present work demonstrates that transition temperature of thermotropic liquid crystal. It is sensitive technique to identify the phase transition temperature of LCs compound. Figure 15 indicted the nematic mesophase of different compound of PCOCCA-n. Here, figure 16 indicated smectic mesophase of present series is juxtaposition with well published research article [19, 20].

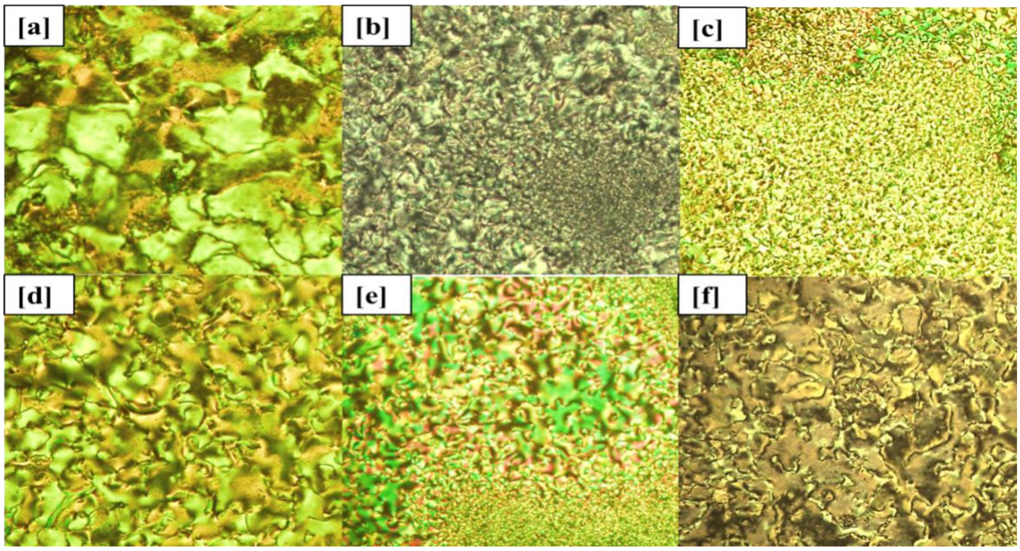

Figure 15: POM optical photomicrographs of (a) Thread like texture of the Nematic phase exhibited by PCOCCA-4 compound (b) texture of the Nematic phase exhibited by PCOCCA -6 compound (c) Thread like texture of the Nematic phase exhibited by D-8 compound (d) Thread like texture of the Nematic phase exhibited by PCOCCA -10 compound (e) Schlieren texture of the Nematic phase exhibited by PCOCCA -14 and (f)Thread like texture of the nematic phase exhibited by PCOCCA -16 compound on heating cycle

The cardinal characteristic of a smectic phase which different from nematic or cholesteric phase. In a smectic A, molecules are aligned perpendicular to the layers, without long-range crystalline ordering within them. In a smectic C, the preferred molecular axis is not perpendicular to the layers, so that the phase has biaxial symmetry.

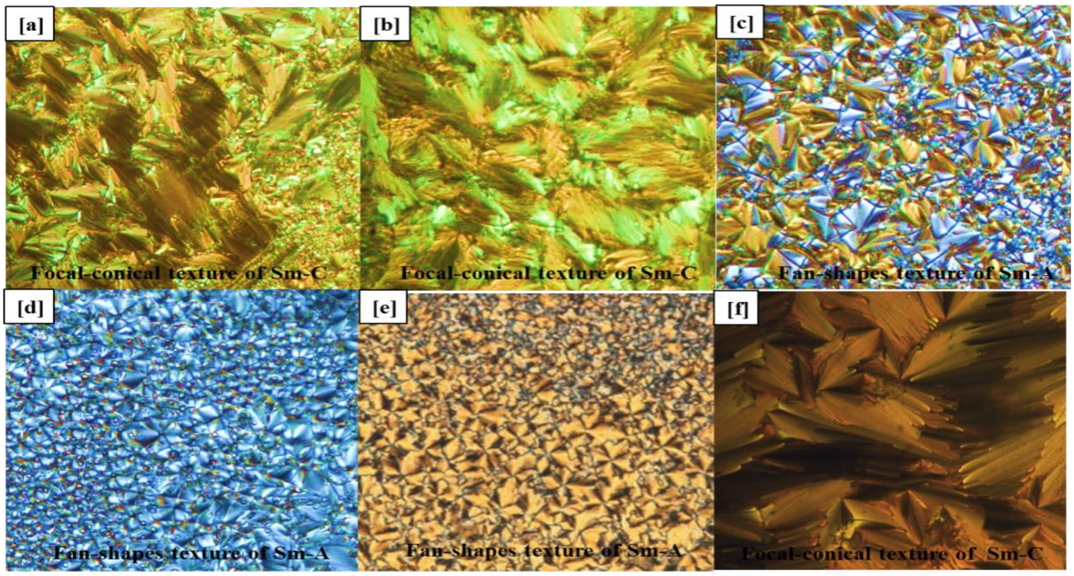

Figure 16: POM optical photomicrographs of (a) Focal conical texture of Sm-C phase exhibited by PCOCCA -14 compound on heating cycle (b) Focal conical texture of Sm-C phase exhibited by PCOCCA -14 compound on cooling cycle (c) Fan-shaped texture of Sm-A phase exhibited by PCOCCA -16 compound on heating cycle (d) Fan-shaped texture of Sm-A phase exhibited by PCOCCA -16 compound on cooling cycle (e) &(f) reported focal conical and fan-shaped smectic phase

V. COMPARISON OF SERIES PCOCCA-N AND STRUCTURALLY SIMILAR SERIES-X

The rigidity and flexibility of proposed LC compounds are changed with the change in flexible chain. The directly relation between geometrical shape compounds and their mesophase behaviour. So, types of terminal group, nature of terminal group and position of substitution such as ortho , meta and para are effected on LC geometrical Orientation and mesophase behaviour of LC compounds.

Homologous series PCOCCA-n and series Xselect for comparative study are similar with terminal end Chloro group , terminal flexible alkyl chain and three phenyl ring[21]. However; differ with respect to central bridge and lateral group. Homologous series PCOCCA-n and series-X differ by central bridge –CH=CH-COO- and –COO- ,-N=N- and –CH=N- and lateral group $–OCH_3$ and –H , $-CH_3$ and –H group respectively, there for flexibility and rigidity of series PCOCCA-n and series –X are different.

Figure8: Comparative molecular structure of the compounds

- ➢ Series PCOCCA-n is partially smectogenic and fully nematogenic, while Series-X partially smectogenic and fully nematogenic in behaviour.
- ➢ Smectogenic behaviour of series PCOCCA-ncommences from the ethyloxy homologue and Smectogenic behaviour of series-X commences from propyloxy homologous.
- ➢ Nematogenic behaviour of series PCOCCA-nand series-X commences from methyloxy homologue.
- ➢ Series PCOCCA-n is fully enantiotropy in nature, while some homologue of series-x is monotropy in nature.

The average transition temperatures of homologue series PCOCCA-n and series-X recorded in table-4.

Table-4: Commencement and Average transition temperature of series PCOCCA-n and series-x

Series →	**PCOCCA-n**	**X**
Smectic-Nematic	124.2 ^{0}C (C_2 & C_{14}-C_{16})	221
Commencement of smectic phase	C_2	C_3
Nematic-Isotropic	139.4 ^{0}C (C_1-C_{16})	253
Commencement of nematic phase	C_1	C_1
Total mesophase length in ^{0}C	3.8 ^{0}C to 64.3 ^{0}C C_1 C_2	4.5^{0}C to123^{0}C C_8C_2

From the table-4 following conclusion are observed that

- ➢ Presented both series are poly mesomorphic in nature with smectic and nematic mesophase.
- ➢ Both series nematic mesophase commencement from C_1 homologue.
- ➢ In series PCOCCA-n commencement of nematic mesophase from C_2 homologue and in series-X commencement of nematic mesophase from C_3 homologue.
- ➢ The thermal stability of series PCOCCA-n is lower than series-X.
- ➢ Total mesophase length of series PCOCCA-n is lower than series-X.

VI. CONCLUSIONS

New series of the compounds were synthesized. The liquid crystal properties of these compounds were investigated. Above study following conclusions are appearance:

- The novel series PCOCCA-nhas smectogenic as well as nematogenic mesophase. The ethyloxy and last two homologues of present series are polymorphic in nature.
- The Comparison of series PCOCCA-n and Series-X, we can conclude that the phenomenon of mesomorphic is totally dependent on structure's flexibility and molecular rigidity.
- The homologue of novel homologous series PCOCCA-n is middle order melting and shorter mesophase length.

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