Confirmation of Phase transitions through Dielectric studies of Liquid Crystals

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Abstract—. The phase transition temperatures and phases in ferroelectric series of 2-(4- *n* alkanoyloxy benzylidenamino) benzothiazoles (where *n*=12 and 16) are studied using polarizing micro scope (POM) and it reveals the occurrence of SmA phase. Dielectric parameter studied as a function of temperature can be used to determine the phase transitions temperature in LCs. The phase transitions are in good agreement with the dielectric studies data.

Keywords— Phase transition, Ferroelectric, Smectic A, Dielectric , Benzothiazoles liquid crystal..

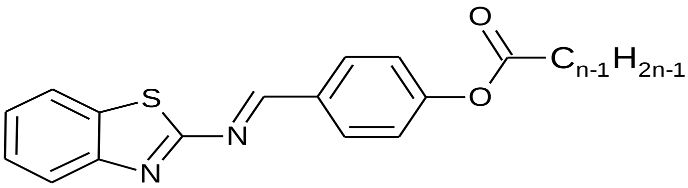
I.INTRODUCTION

Molecular order in liquid crystal phases depends mainly on the mesogenic core structure, its geometry, polarizability, molecular conformation, length-to-breadth ratio as well as the number and the position of permanent dipole moments in the core [1].Interest in the study of mesomorphic heterocyclic has dramatically increased in the recent years due to their wider range of structural templates as well as their optical and photochemical properties [2]. The significance of the heterocyclic core in determining and the properties of liquid crystals have been reported in a series of review papers [3]. Heterocyclic liquid crystals can be synthesized into high dielectric biaxiality that it is built into the compact core unit which is essential in technological devices. These materials possess great potential application in spatial light modulation, all-optical signal processing, optical information storage, organic thin-film transistors, fast switching ferroelectric materials, fluorescent probes for the detection and analysis of biomolecules [4-7]. Heterocyclic mesogens are usually incorporated with hetero atoms, such as N, O and S, resulting in a reduced symmetry in the overall molecule as well as the generation of a stronger polar induction. The inclusion of the heteroatom can considerably change the polarity, polarizability and to a certain extent the geometry of a molecule, thus influencing the type of mesophase, the phase transition temperatures, dielectric constants and other properties of the mesogens [8]. Examples of liquid crystals with incorporated heterocyclic rings are pyridine [1], thiophene [9], oxadiazole [10] and benzoxazole [11-12]. Although many compounds containing a heterocyclic core exhibit mesomorphic properties, mesogenic examples which are derived from benzothiazole are relatively rare. Therefore, the benzothiazole ring is chosen as the mesogenic core in this study.Conventionally, liquid crystalline organic compounds have been widely used as materials in liquid crystal displays. Recently, a few series of smectic reactive benzothiazole mesogens having non-conjugated diene end groups have been reported owing to their potential light-emitting and charge-transporting behavior in organic light-emitting devices (OLEDs) [13]. Besides that, assembling in smectic liquid crystalline phase can also induce the overlapping of aromatic cores, hence facilitating the hopping of charge carriers between the molecules. Owing to this phenomenon, Hanna and co-workers also studied carrier transport properties of some smectic benzothiazole liquid crystalline derivatives [14-18]. Thus, based on the above mentioned interesting results, this has prompted us to study benzothiazole- based liquid crystals..The dielectric studies on two new homologous series of liquid crystals consisting of a benzothiazole core and their liquid crystalline properties were also investigated.

II. EXPERIMENTAL

2-(4- *n* alkanoyloxybenzylidenamino) benzothiazoles (where *n*=12 and 16) mesogens are synthesized and procured from Universiti Tunku Abdul Rahman,Jalan Universiti, Bandar Barat, 31900 Kampar, Perak., Malaysia[19]. Chemical structure of the compound is given below. The samples are filled in LC1 ITO coated liquid crystal cells, 90° twist aligned (5mm X 5 mm X 6 μm) obtained from M/s Instec. USA. Through capillary action method the compounds in their isotropic state are filled in these cells [20]. The temperature and frequency dependence of Capacitance C, Resistance R, Inductance L are measured by using Newton's 4th Ltd., LCR meter model. In this study the cells filled with pure and nano doped samples are placed in an Instec hot and cold stage (HCS

302) equipped with microscope (Olympus BX50) having DP10 camera setup. The temperature is monitored and controlled through a computer by a software program to an accuracy of ± 0.1ºC. The sample is heated to isotropic state and held until to attain thermal equilibrium. The data of C, L and R is taken during cooling process. The measuring signal is the square form with amplitude of 2V. The frequency range of measurement is from 100Hz to 1 MHz.



III. Results and Discussions

Textural & Phase Transition Studies:

Textural and phase transition temperature measurements are made by the polarizing optical microscope (POM) (Olympus BX50) with attached DP10 camera setup and computer controlled HCS 302 hot stage of Instec, USA. The phase transition studies are also carried out for confirmation by using Differential Scanning Calorimeter of TA instruments model DSC Q2000 V24.4 at a scan rate of 5ºC/min. The textural observations of 2-(4- *n* alkanoyloxybenzylidenamino) benzothiazoles (where *n*=12 and 16) made through POM have shown enantiotropic smectic A phase as shown in Plate 1 The transition temperatures and their mesophases were also determined by differential scanning calorimetry techniques. The data of the phase transition temperatures measured from both POM and DSC are in good agreement [19].

For 12 BABTH $\mathbf{Cr} \xleftrightarrow{353.8} \mathbf{Sm\ A} \xleftrightarrow{358.6} \mathbf{Iso}$

For 16 BABTH $\mathbf{Cr_1} \xleftrightarrow{337.9} \mathbf{Cr_2} \xleftrightarrow{352.5} \mathbf{Cr_3} \xleftrightarrow{360.3} \mathbf{Sm\ A} \xleftrightarrow{365.3} \mathbf{Iso}$

(Note: Iso = Isotropic, SmA = Smectic A, Cr = Crystal).

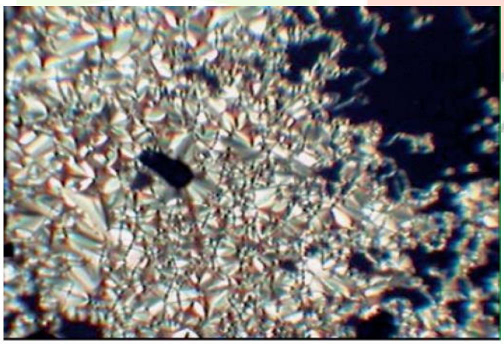
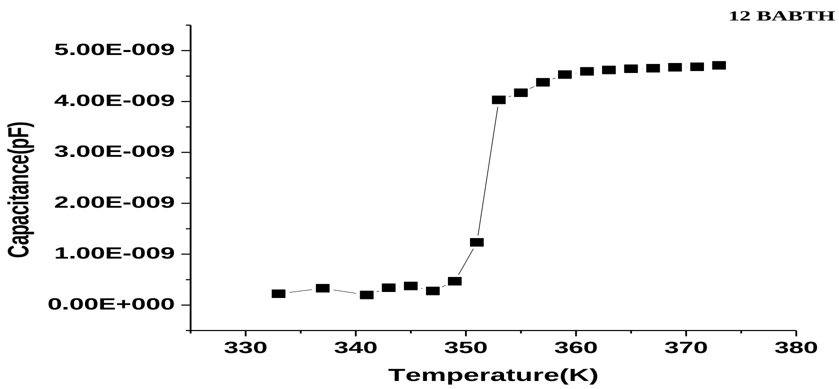
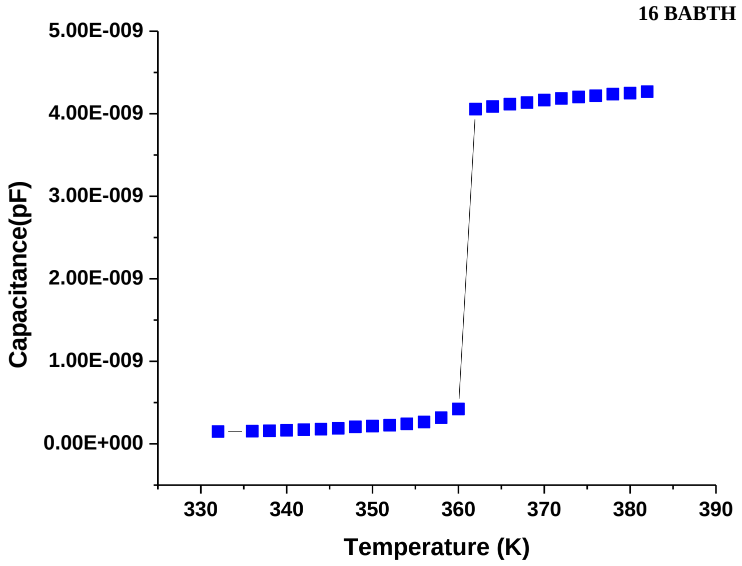


Plate1: Smectic behavior exhibiting 16 BABTH



(a)



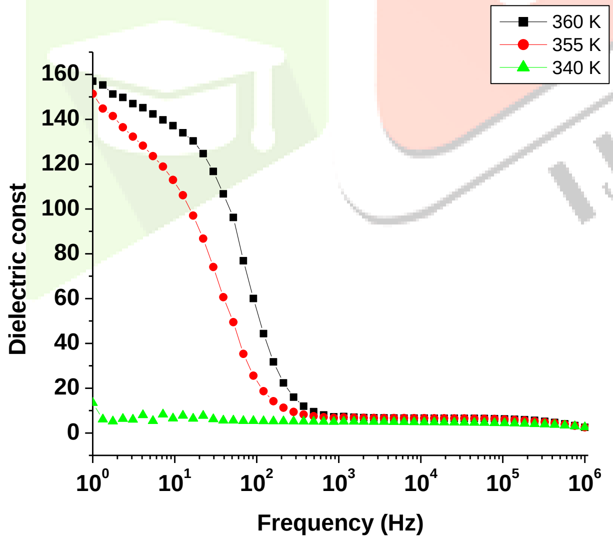
(b)

Figure 1. Variation of capacitance with Temperature (K) for (a) 12BABTH,(b)16BABTH

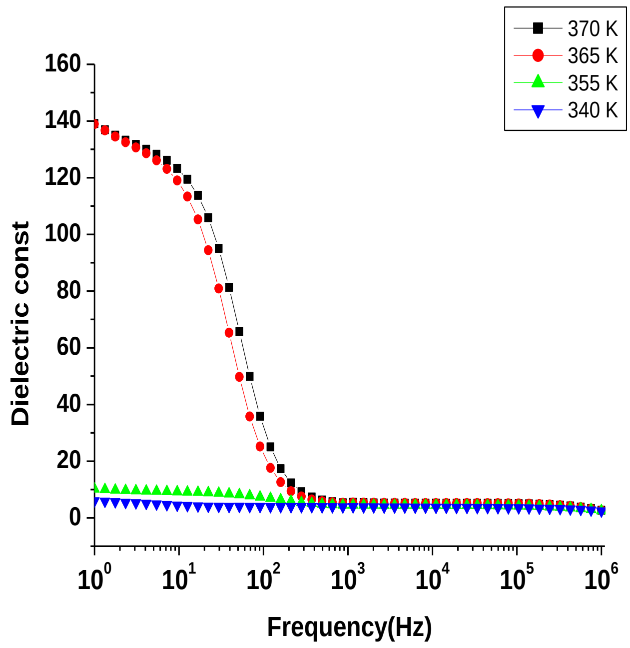
From the figure 1 it is observed that the value of capacitance remain almost constant up to solid phase and vary slightly when the transition from solid to Smectic A has been reached and the value changes sharply when isotropic state has reached. So, the transition temperatures mentioned in above are confirmed from this data also.

Low frequency Dielectric studies:

Variation of dielectric constant, temperature coefficient dielectric constant, dielectric loss a function of frequency, for 12 BABTH and 16 BABTH mesogens at different phases are is calculated from equations from 2.80 to 2.84 and the outcome results are shown in figure 2 and 3

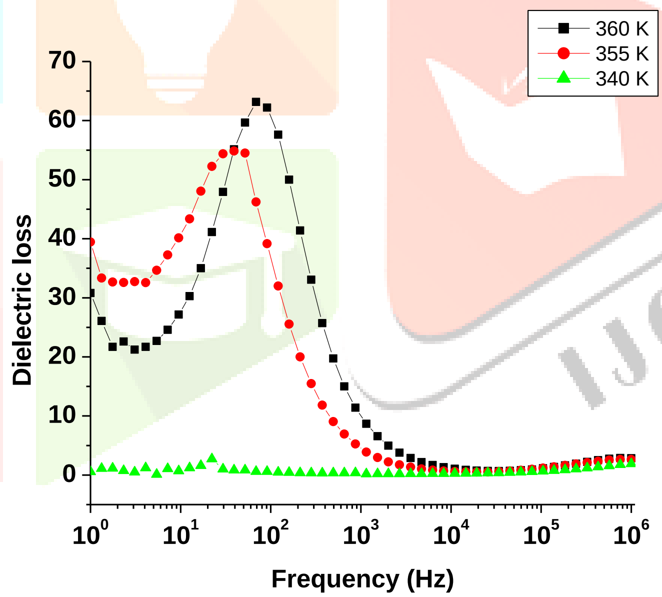


(a)

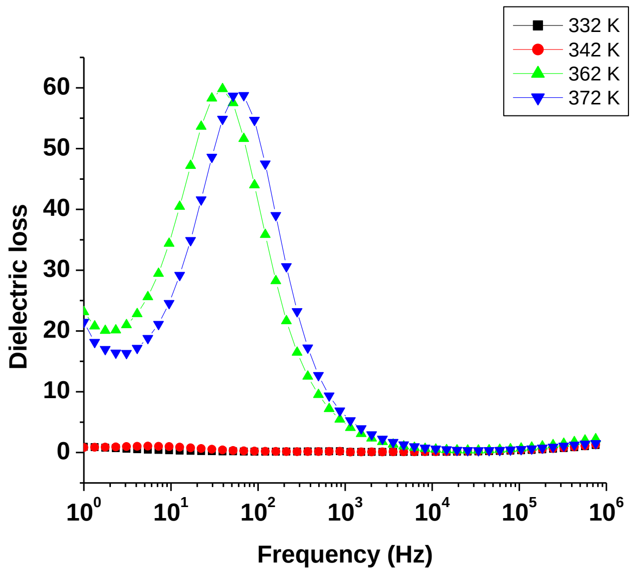


(b)

Figure 2: Dielectric constant ε^1 versus frequency f, for 12 BABTH and 16 BABTH mesogens (a,b) at different phases.



(a)



(b)

Figure 3 Imaginary part of Complex permittivity ε^{11} versus frequency f, for 12 BABTH and 16 BABTH) mesogens (a,b) at different phases.

The temperature variation of permittivity is not associated with any abrupt change in the vicinity of any of the phase transitions, as observed in some other LCs [24-26]. From the figure 2 it is clear that, at high frequency both the compounds exhibits almost constant ε′ showing lower values generally being associated with the lowest electrical loss characteristics. Due to the high orientation of liquid crystal molecules in isotropic phase shows high value of ε′ when it is compared with other phases. From Table.1 it is evident that the decrease in permittivity with frequency can be explained on the basis of Koop's theory [27], which considers the dielectric structure as an inhomogeneous medium of two layers of the Maxwell–Wagner type [28]. In this model, the dielectric structure is assumed to be consisting of well conducting grains which are separated by poorly conducting grain boundaries. At lower frequencies the grain boundaries are more effective for conductivity and permittivity than grains [29]. Therefore, permittivity is high at lower frequencies and decreasing as frequency increases. The decrease in permittivity takes place when the jumping frequency of electric charge carriers cannot follow the alternation of the applied a.c. electric field beyond a certain critical frequency.

Table.1.Variation of dielectric constant with frequency at differen temperatures

	Dielectic constant					
	12 BABTH			16 BABTH		
Frequency	Temperature (K)					
(Hz)	360	355	340	370	365	355
1	157.0204	151.3745	13.44807	139.1114	138.9301	10.18129
1.33	155.2878	144.7735	6.06769	136.9332	136.7119	9.99987
1.76	151.2778	141.4489	5.18835	134.964	134.5398	9.8099
2.33	149.7382	136.4609	6.3223	133.2061	132.5361	9.66037
3.09	147.016	132.2388	5.98569	131.7317	130.6714	9.58409
4.09	145.1977	128.2476	7.9677	130.0302	128.6041	9.49367
5.43	142.3765	123.5578	5.37125	128.251	126.1241	9.39809
7.2	139.7375	118.878	8.29761	126.116	123.107	9.3183
9.54	137.1557	112.9338	6.52994	123.2944	119.0223	9.22259
12.6	133.9942	106.1272	7.71829	119.4229	113.359	9.13945
16.8	130.3591	97.03675	6.41539	113.7809	105.2828	9.01277
22.2	124.7164	86.75621	7.6689	105.8885	94.41832	8.87738
29.5	116.7358	74.09162	6.18461	95.05871	80.92697	8.69992
39.1	106.7255	60.62061	5.56893	81.35105	65.30148	8.46781
51.8	96.2119	49.48313	5.5688	65.70174	49.73515	8.17562
68.7	76.9029	35.32217	5.37137	49.85345	35.78318	7.80278
91	60.00774	25.59521	5.39525	35.83196	25.19874	7.37947
121	44.37225	18.67297	5.27948	25.03778	17.62369	6.89365

160	31.72091	14.17457	5.2465	17.33316	12.59328	6.37077
212	22.35008	11.26014	5.21773	12.31863	9.41852	5.85701
281	16.01025	9.40724	5.17694	9.20593	7.56532	5.42467
373	11.95425	8.23199	5.14809	7.36927	6.4918	5.07617
494	9.49176	7.50324	5.10748	6.30029	5.8697	4.82104
655	8.05118	7.048	5.05978	5.68154	5.50544	4.64763
869	7.22073	6.74988	5.00016	5.3284	5.29583	4.52808
1150	7.34772	6.94357	5.10994	5.47691	5.42467	4.53336
1530	7.04072	6.83141	5.08047	5.34141	5.35185	4.49283
2020	6.85901	6.76189	5.04629	5.27188	5.30815	4.46725
2680	6.75286	6.71106	5.01144	5.22812	5.28405	4.45053
3560	6.68807	6.67608	4.97523	5.20113	5.26906	4.44107
4710	6.65097	6.65312	4.93722	5.18371	5.25317	4.43286
6250	6.62494	6.63478	4.89674	5.17396	5.24435	4.42619
8290	6.60549	6.61225	4.85638	5.16527	5.24087	4.41934
11000	6.59368	6.59399	4.81508	5.15869	5.2343	4.41399
14600	6.58225	6.57948	4.77199	5.15279	5.22778	4.40686
19300	6.56722	6.55493	4.72807	5.14667	5.2232	4.39675
25600	6.55133	6.5292	4.68298	5.14	5.21469	4.3827
33900	6.53181	6.49002	4.63703	5.13032	5.20408	4.36411
45000	6.50176	6.43445	4.58607	5.11348	5.18908	4.33835
59600	6.45495	6.3569	4.52851	5.09187	5.16502	4.3023
79100	6.3861	6.24288	4.4612	5.05714	5.12845	4.25343
105000	6.28271	6.08663	4.38086	5.00446	5.07023	4.18938
139000	6.12836	5.88464	4.2846	4.92972	4.9878	4.10757
184000	5.90898	5.62407	4.16941	4.82036	4.87169	4.00743
244000	5.60274	5.29355	4.02575	4.6638	4.70376	3.87946
324000	5.20845	4.90264	3.85828	4.45975	4.48188	3.72827
429000	4.70597	4.43919	3.65116	4.18195	4.18901	3.54144
569000	4.07444	3.87989	3.37768	3.79506	3.79014	3.29378
754000	3.33939	3.23735	3.01791	3.28868	3.27608	2.96596
1000000	2.54078	2.52572	2.55846	2.67525	2.66175	2.53525

The figure 3 indicates the dielectric loss for 12 BABTH and 16 BABTH mesogens low dielectric loss at high frequencies showing similarity with that of the variation of dielectric constant (figure.2) on owing to smaller angle of rotation. From the Table.2it is clear that the loss factor on frequency dependent is also same in as similar way as the dielectric constant (which is known when the loss experimental data was analyzed). The variation in presence of relaxation peaks is observed for both the compounds within the frequency range covered.

Table.3A.2 Variation of dielectric loss with frequency at different Temperatures

	Dielectic loss					
	12 BABTH			16BABTH		
Frequency	Temperature (K)					
(Hz)	360	355	340	372	362	342
1	30.81682	39.4497	0.55324	21.47689	23.12908	0.82217
1.33	26.08525	33.34858	1.0914	18.16914	20.77473	0.87543
1.76	21.70081	32.6747	1.13298	16.99348	20.05989	0.88021
2.33	22.591	32.59914	0.74173	16.4028	20.1256	0.92841
3.09	21.21882	32.72911	0.48214	16.33927	20.99627	0.98214
4.09	21.69398	32.5736	1.20607	17.19385	22.80022	1.01205
5.43	22.70479	34.65055	0.0918	18.81061	25.59689	1.05852

7.2	24.58402	37.26468	1.05629	21.12641	29.43366	1.02909
9.54	27.16505	40.14909	0.69642	24.56591	34.37721	0.97411
12.6	30.28402	43.35507	1.20884	29.19322	40.46009	0.88874
16.8	35.01707	48.0526	1.59519	34.92482	47.18671	0.77793
22.2	41.13023	52.255	2.7151	41.61866	53.62961	0.6482
29.5	47.93054	54.3788	1.00141	48.623	58.28199	0.53472
39.1	55.14398	54.84347	0.83205	54.87342	59.82595	0.43027
51.8	59.65234	54.49082	0.835	58.67606	57.51373	0.33551
68.7	63.15574	46.23671	0.58011	58.77845	51.6244	0.28087
91	62.20402	39.15811	0.59105	54.69358	43.98943	0.23492
121	57.62181	31.99426	0.45872	47.50676	35.84482	0.1982
160	49.98898	25.54541	0.41624	39.03275	28.23413	0.1733
212	41.39457	19.998	0.37021	30.62229	21.64189	0.15641
281	33.06437	15.4721	0.34189	23.22866	16.46744	0.15012
373	25.72075	11.84007	0.33179	17.25196	12.51554	0.15192
494	19.74002	9.04816	0.33631	12.72223	9.50246	0.16113
655	15.00256	6.93918	0.34412	9.36084	7.18459	0.17516
869	11.39864	5.24857	0.35559	6.89526	5.4457	0.19166
1150	8.68134	3.88388	0.18478	5.27405	4.07848	0.08856
1530	6.56955	2.9634	0.19083	3.96925	3.08952	0.09378
2020	4.97594	2.23413	0.19744	2.9782	2.33383	0.10159
2680	3.77991	1.7291	0.20559	2.24897	1.75732	0.10733
3560	2.87507	1.34416	0.21607	1.71147	1.33797	0.11311
4710	2.19602	1.04314	0.22622	1.3057	1.03556	0.12014
6250	1.694	0.82842	0.23613	0.99822	0.80579	0.12783
8290	1.32189	0.68265	0.24927	0.77227	0.6332	0.13614
11000	1.05301	0.58524	0.26402	0.60939	0.51403	0.14548
14600	0.86846	0.52739	0.28179	0.49417	0.43404	0.15778
19300	0.75208	0.51338	0.3054	0.41734	0.38665	0.17365
25600	0.69044	0.53289	0.33538	0.37267	0.36925	0.19317
33900	0.6812	0.591	0.37234	0.35452	0.37642	0.21853
45000	0.72098	0.68527	0.42156	0.36361	0.41284	0.25018
59600	0.80906	0.81737	0.48392	0.39757	0.47751	0.29199
79100	0.94642	0.98269	0.56091	0.45626	0.57151	0.34396
105000	1.13227	1.17861	0.65284	0.53917	0.69503	0.40681
139000	1.36264	1.3969	0.75915	0.64635	0.84907	0.48067
184000	1.63271	1.63413	0.88125	0.77838	1.03421	0.56701
244000	1.92841	1.87545	1.01896	0.92894	1.24734	0.66774
324000	2.22885	2.10907	1.17515	1.09549	1.48162	0.78581
429000	2.52151	2.33648	1.35779	1.2763	1.74284	0.931
569000	2.75762	2.52588	1.56221	1.43822	2.00461	1.10559
754000	2.87411	2.63391	1.76315	1.52085	2.21744	1.29909
1000000	2.83958	2.63155	1.90999	1.44258	2.31503	1.47755

Data of Dielectric loss clearly shows that low frequency data are affected due to ionic conductance, where as high frequency data are affected due to ITO resistance [21]. As usual relaxation frequencies are seen to shift towards lower side with decrease in temperature.

CONCLUSIONS

The phase transition temperatures and phases in ferroelectric series of 2-(4- *n* alkanoyloxy benzylidenamino) benzothiazoles (where *n*=12 and 16) are studied using polarizing micro scope (POM) Thermal microscopic studies could reveal the occurrence of SmA phase in the materials were studied. Dielectric parameter studied as a function of temperature can be used to determine the phase transitions temperature in LCs. Although, a phase transition is not accompanied with an abrupt change in dielectric parameter, the anomaly associated with its temperature derivative could be a tool to identify the phase transitions involving LC phases the relaxations peaks and activation energies were observed at different temperatures as a function of frequency for both the samples.

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