

# A NOVEL DIELECTRIC TECHNIQUE FOR THE CRYSTALLIZATION KINETICS STUDY OF A LIQUID CRYSTALLINE COMPOUND

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*This paper is dedicated to the memory of late Prof. Dr. S. Palanichamy*

The crystallization kinetics of a newly synthesized ferroelectric liquid crystal was studied by two techniques viz., the traditional thermal analysis and the present technique which involves electrical studies, namely, capacitance and dielectric loss variation with time at specific predetermined temperatures. In the traditional thermal technique, thermograms were run from crystallization temperature to the isotropic melt for different time intervals while in the present technique, the liquid crystal sample was held at a specific crystallization temperature, and the variation of capacitance and dielectric loss with time are noted. From the results obtained from both the techniques, the rate of crystallization of smectic ordering in a newly synthesized ferroelectric liquid crystal was discussed in relation to the kinetophase. Further, the molecular mechanism and dimensionality in the crystal growth were computed from the Avrami equation. The present technique is compared with the traditional thermal technique and the merits were discussed.

*Key words:* Differential scanning calorimetry; kineto phase optical textures.

## 1. INTRODUCTION

Liquid Crystals are those which exhibit anisotropic property of solids as well as fluidity of isotropic liquid and made up of rod like molecules. The rod-like shaped molecules, which can be obtained by joining the two or more phenyl rings or cyclohexyl rings with a relatively rigid bridging group and attached with flexible aliphatic end chains, when self assembled into a molecular organized structures with long range. Orientational order show anisotropy as well as fluidity as a function of temperature and they are called as Liquid Crystals [1]. Study of crystallization kinetics [2,3] is a powerful tool to understand the various mechanisms involved in crystallization of liquid crystals. Regarding the crystallization kinetics study, in the literature till date, other than thermal analysis there were no reports of any other methods to analyze and study this interesting phenomenon.

The author presents a novel dielectric technique to understand the phenomenon of crystallization kinetics. In continuation of our experimental studies [4,5] on nO.m and ferroelectric liquid crystals (FLC), a detailed analysis of a newly synthesized ferroelectric liquid crystal, dodecyl{4-(3-(4-hippuratoxy phenyl)-2-choloro-1-oxy-propanyl) benzoate is presented.

## 2. EXPERIMENTAL

### 2.1. THERMAL ANALYSIS

The ferroelectric liquid crystal mesogen of the present investigation was synthesized and characterized as reported earlier [5]. The crystallization kinetics of the present compounds, determined by the rate of growth of a particular transition, were performed on a Shimadzu DSC-60 differential scanning calorimeter and Agilent 4192A LF impedance analyzer. The thermo grams at each crystallization temperature, together with simultaneous phase identification [6] were obtained using a Instec Standalone Temperature Controller (STC 200) supplemented by Nikon polarizing microscope. The DSC measurements were performed on FLC compound (3 mg sample) using aluminum and/or glass crucibles. A typical DSC scan for a given sample at each crystallization temperature is described as follows.

The sample was heated to its isotropic melt with a scan rate of  $10^{\circ}\text{C min}^{-1}$ ; after holding for 1 minute to attain thermal equilibrium, the sample was cooled at the same scan rate to its predetermined crystallization temperature. After holding for a requisite time interval at crystallization temperature, the endothermic peaks were recorded while the sample was cooled to the crystal state at of  $10^{\circ}\text{C min}^{-1}$ .

### 2.2. DIELECTRIC ANALYSIS

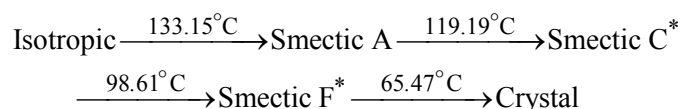
For the elicitation of the dielectric data, the FLC sample under investigation was filled in a polyamide buffed cells (Instec Inc. USA) in its isotropic state under vacuum. Silver paste and wires were used to draw the electrodes from the cell. The cell was placed in a Instec hot and cold stage (HCS402) equipped with Instec Standalone Temperature Controller (STC 200). The temperature is monitor and controlled through a computer by a software program to an accuracy of  $\pm 0.01^{\circ}\text{C}$ .

The sample was heated to its isotropic melt with a scan rate of  $10^{\circ}\text{C min}^{-1}$ ; after holding for a period of 1 minute time to attain thermal equilibrium, the sample was cooled at the same scan rate to its predetermined crystallization temperature. Simultaneous textural observation through polarizing microscope is also made to ascertain the isotropic phase of the sample. After holding for a requisite time interval at crystallization temperature, the data of capacitance and dielectric loss was noted for each time interval.

### 3. RESULT AND DISCUSSION

#### 3.1. PHASE IDENTIFICATION: POLARIZING MICROSCOPIC STUDIES

The phase variants and their transition temperatures were determined from the characteristic textural observations [6] under crossed polars of a polarized microscope. The ferroelectric liquid crystal dodecyl{4-(3-(4-hippuratoxy phenyl)-2-chloro-1-oxypropanyl) benzoate exhibited focal conic fan texture in smectic-A phase while the smectic-C\* phase is identified as focal conic with concentric striations. Further decrease of temperature resulted in a broken focal conic texture manifesting the higher order smectic F\* phase. The general phase variants of the present compound with respective transitions temperatures can be represented as:



In the buffed cell containing the sample, the focal conic texture is observed in green colour. An interesting observation is that, when an electric stimulus is applied to the buffed cell, the colour of the texture turns to red indicating the presence of the field. This result is in concurrence with our previous reported data [4] on ferroelectric liquid crystals.

#### 3.2. SELECTION OF THERMAL RANGE OF CRYSTALLIZATION TEMPERATURES

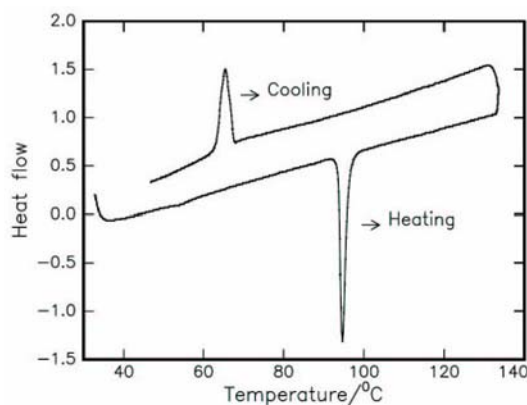


Fig. 1 – DSC heating and cooling thermo grams of FLC recorded at a scan rate of  $10^{\circ}\text{C min}^{-1}$ .

The procedure for the thermal selectivity for the crystallization temperatures (CT) is described as follows. The DSC thermo gram of the FLC is illustrated in Figure 1. The compounds exhibits two distinct transition in the heating run at  $94.66^{\circ}\text{C}$  and  $133.15^{\circ}\text{C}$  with heat of transition  $18.21 \text{ mJ/g}$  and  $5.84 \text{ mJ/g}$  respectively. The former transitions is referred as  $T_{\text{cr-melt}}$ , the latter as  $T_{\text{SmF}^*-\text{Iso}}$ . Upon cooling, the transitions  $T_{\text{Iso-SmA}}$ ,  $T_{\text{SmA-SmC}^*}$ ,  $T_{\text{SmC}^*-\text{SmF}^*}$  and  $T_{\text{SmF}^*-\text{Cr}}$ , are observed at  $133.15^{\circ}\text{C}$ ,

119.19°C, 98.61°C and 65.47°C with heat of transition 3.27 J/g, 0.01 J/g, 0.13 J/g and 5.25 J/g. However the DSC peaks at 133.15°C and 119.19°C manifesting Isotropic to smectic A and Smectic A to Smectic C\* are not well resolved. From this data it is inferred that the thermal span of mesomorphic phase is 65.47°C. Once the  $T_{\text{SmA-SmC}^*}$  is completed the kinetics of crystallization from smectic F\* could be investigated over a temperature range between  $T_{\text{SmC}^*-\text{SmF}^*}$  and  $T_{\text{SmF}^*-\text{Cry}}$ , provided if the crystallization kinetics are not too fast.

### 3.3. CRYSTALLIZATION KINETICS THROUGH DSC

The crystallization kinetics of FLC relating to the phase transition from Smectic F\* to the melt is selectively performed at each predetermined crystallization temperatures viz 89, 84, 83, and 78°C. The sample is held at 78°C for different time intervals (0.1 to 7 minutes). The heating curve with a crystallization time of  $t = 0$  min is recorded immediately following the quenching of the crystal to melt, at crystallization temperature 89°C. This curve displays only smectic C\* to isotropic endoderm indicating that the Smectic C to Smectic F\* transition has not yet occurred. However in small increment of time at  $t = 0.1$  min the appearance of a small peak is attributed to a Smectic C to Smectic F transition suggesting fast crystallization.

The enthalpy values for individual transitions at different time intervals are calculated at each crystallization temperature using the software of Shimadzu DSC-60, and the corresponding data plotted against the corresponding logarithm of time intervals. These plots have an identical shape, apart from the shift in the log  $t$  axis suggesting the limitations of the rate of crystallization kinetics [7]. Furthermore, simultaneous measurement of the heats of melting of the smectic F endoderm with time shows, with out ambiguity, that the affective beginning and end of the crystal formation process coincide with those of the decay of smectic F phase, illustrating a direct smectic C to crystal phase conversion.

Table 1

Transition temperatures (in °C) obtained from thermal microscopy (TM), DSC and dielectric studies of FLC compound. Corresponding enthalpy values (in J/g) are given in parenthesis

Compound	Phase Transition	TM	DSC	Dielectric studies	
				Capacitance	Dielectric loss
FLC	I <sub>SO</sub> -Sm A	134.1	133.15 (3.27)	134.5	134.4
	Sm A-Sm C*	120.2	119.19 (0.01)	120.7	120.6
	Sm C-Sm F*	100.6	98.61 (0.13)	100.1	100.1
	Sm F*-Crystal	67.6	65.47 (5.25)	68.1	68.0

A plots of heats of melting of the mesomorphic phase viz. the log of annealing time for different crystallization temperatures obtained by shifting data along the log t axis to the 78°C curve called a master curve strongly suggest that the same mechanism operates for all the crystallization temperatures. As expected [7], the overall crystallization rate is controlled by a nucleation rate influencing the rate of growth of domains, this is a function of the degree of super cooling and the starting smectic mesophase. The corresponding data of crystallization time  $t^*$  along with the calculated crystal growth parameters for different crystallization temperatures are summarized in table 2, which includes the results relevant to the following sections.

Table 2

Measured crystallization parameters for 63.2% transformation from the various smectic mesophases to the crystalline phase of FLC compound experimentally obtained by thermal and electrical studies

Sample	CT /°C	Thermal studies			Electrical studies					
		Differential Scanning Calorimetry ( $\Delta H$ )			Dielectric studies (1 KHz)					
					Permittivity ( $\epsilon'$ )			Dielectric loss ( $\epsilon''$ )		
		t*/sec	n	b	t*/sec	n	b	t*/sec	n	b
FLC	89	25.12	0.534	0.598	24.60	0.154	0.447	17.78	0.447	0.517
	84	49.24	0.612	0.489	38.01	0.365	0.363	35.4	0.312	0.450
	83	61.12	0.589	0.394	39.10	0.244	0.246	39.80	0.463	0.445
	78	63.81	0.598	0.302	43.65	0.194	0.151	52.58	0.017	0.312

### 3.4. CRYSTALLIZATION KINETICS THROUGH DIELECTRIC STUDIES

We propose that the crystallization kinetics can also be studied and analyzed at a selected frequency with the dielectric data. The crystallization kinetics relating to the phase transition from Smectic  $F^*$  to the melt of FLC is selectively performed at each predetermined crystallization temperatures viz., 89, 84, 83, and 78°C at an excitation frequency of 1 KHz. The sample is held at 78°C for different time intervals (0.1 to 10 minutes). The dielectric data (capacitance and dielectric loss) at 1 KHz excitation frequency with a crystallization time of  $t = 0$  to 10 min are recorded immediately following the quenching of the crystal to melt, at crystallization temperature 78°C. The capacitance and dielectric loss values for individual transitions at different time intervals are noted at each crystallization temperature.

### 3.5. THE PROCESS OF CRYSTALLIZATION

In general, the kinetics of crystallization involving the rate of growth of small domains in a smectic phase is manifested equally by its temperature and time. Temperature dependence of nucleation, taking place as a homogenous process over a constant period of time leads to the phenomenon of sporadic growth. In addition,

defects and impurities in the compound have a pronounced influence on the nucleation process [7]. Further contributions from solid state transformations, where growth occurs only at the surface of the nuclei, hampers the overall rate of phase transformation and the dimensional geometry of the growing domains.

It is well known that the crystallization process involving the fraction of the transformed volume  $x$ , at a time  $t$  measured since the beginning of the crystallization process, is described by Avrami equation [2,3]

$$x = 1 - \exp(-bt^n) \quad (1)$$

where the constant  $b$  and  $n$  depend on the nucleation mechanism and the dimensionality geometry of the growing domains, respectively. The transformed volume  $x$  at a crystallization time  $t$  is given by  $\Delta H/\Delta H_0$ , where  $\Delta H$  is the crystal heat of melt measured at time  $t$  and  $\Delta H_0$  is the maximum value obtained from the plateau of the individual master curves. Similar argument holds good for dielectric data  $\Delta\epsilon'/\Delta\epsilon'_0$  and  $\Delta\epsilon''/\Delta\epsilon''_0$  where  $\Delta\epsilon'$  and  $\Delta\epsilon''$  are the values of capacitance and dielectric loss at time  $t$  and  $\Delta\epsilon'$ ,  $\Delta\epsilon''_0$  are the maximum value obtained from the plateau of the individual master curves.

If the kinetics of the crystallization from the corresponding smectic phases are described by above Avrami equation, the data for all the crystallization temperatures can be applied to the single equation

$$x = 1 - \exp[1 - (t/t^*)^n] \quad (2)$$

where  $t^* = b^{-1/n}$ . Further, the characteristic time  $t^*$  can be experimentally determined, since at  $t = t^*$ ,  $x = 0.632$ . Substituting the values of  $t^*$  and  $x$  in equation (1), constants  $b$  and  $n$  are obtained at a specified crystallization temperature. It is found from the experimental data that the constant  $n$  which manifests the dimensional geometry of the growing domains is almost unaltered while the magnitude of the constant  $b$ , which govern the nucleation mechanism, varies minutely for the FLC compound studied. The data of constants  $n$  and  $b$  experimentally obtained by DSC and dielectric studies (capacitance and dielectric loss) for various specified crystallization temperatures of the present compound are tabulated in the Table 2.

For a specified crystallization temperature, the values of constants  $n$  and  $b$  are found to be unaltered in both thermal and electrical studies implying that the same type of nucleation mechanism is taking place in the present compound. The trend of the magnitude of the two constants  $n$  and  $b$  are found to be in agreement with the data reported for discotic [7] and smectic [8] mesophases.

### 3.6. INFLUENCE OF TILTED SMECTIC F\* PHASE VARIANT ON CRYSTALLIZATION KINETICS

The phase sequence in liquid crystal molecules has a pronounced influence on their crystallization kinetics. The kinetic phase which occurs prior to the

crystallization, is solely responsible for many combinational factors of the crystallization mechanism. In the present study of FLC compound the kineto phase prior to crystallization is Smectic F\*. Our previous studies [9] on different nO.m compounds exhibiting various kineto phases concurred with data of the present investigations. Further, in Smectic F\*, as expected, the rate of crystallization is rapid as it is close to crystalline phase. It is a known fact that crystallization kinetics will be fast for the *crystallization temperatures* (CT) near to crystal and slow when the CT is near the isotropic melt.

### 3.7. INFLUENCE OF EXCITATION FREQUENCY ON THE CRYSTALLIZATION KINETICS

In the present study it is found that the excitation frequency given to the sample plays a vital role in determination of the crystallization kinetic study. The compound under study is excited by a frequency of 1 KHz and the resultant capacitance and dielectric loss with time are noted. The resolution of the dielectric spectrum depends on the input excitation frequency. When the same experiment is tried at other higher frequencies the resolution the dielectric spectrum is minimal. Hence it is observed that there is a threshold frequency, in this case 1 KHz, where the sample can be tested. In fact, from our experiments with various liquid crystalline samples, we observed that this threshold frequency depends on the nature of the sample. In the homologous series N-(p-nalkoxybenzylidene)-p-alkylaniline which are Schiff's bases, the threshold frequencies varies between 500 Hz to 1 KHz.

### 3.8. INFLUENCE OF CONSTANT $b$

The constant  $b$  has a direct influence on the nucleation mechanism. It is found in this study that constant  $b$  has smaller values as the crystallization temperatures decreases. The value of logarithm  $b$  obtained by thermal and dielectric studies plotted against various crystallization temperatures is depicted in Figure 2 along with respective

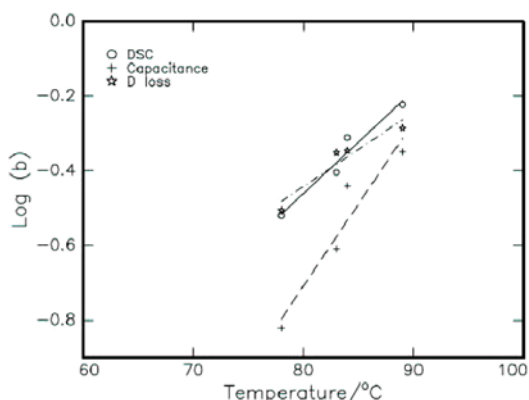


Fig. 2 – The logarithm of the constant  $b$  obtained by thermal and dielectric techniques as a function of crystallization temperatures.

linear fits. The linear nature of the curve strongly implies a unique nature of the crystallization process. It is interesting to point out, though the numerical values of constant  $b$  obtained by two techniques vary, the slope of the fit is almost identical, implying the fact the crystallization processes in both thermal and electrical techniques is uniform and identical. From table 2 it can be observed that  $b$  is inversely proportional to crystallization times  $t^*$  and directly proportional to constant  $n$ .

#### 4. MERITS OF THE DIELECTRICAL TECHNIQUE

The following are the merits of the novel technique:

- i) In this present study crystallization kinetics data can be simultaneously studied through variation of capacitance and dielectric loss in time domain and correlation of these results can be computed.
- ii) Compared to the traditional thermal technique of DSC where different runs are required for each time interval, in the present technique, the data of  $\epsilon'$  and  $\epsilon''$  for different time can be obtained in a single run. This reduces the time and importantly acquires the data in a single stretch.
- iii) Perfect alignment of the sample in the cell can be obtained as electric field (*bias*) can be given through out the study.
- iv) Simultaneous textural observation of the compound through polarizing microscope enables for optical textural correlation of the data.
- v) Data from the impedance analyzer can be accurately obtained through HPIB interface and analyzed using LabVIEW platform, minimizing the errors.

#### 5. CONCLUSIONS

1. A novel dielectric technique is presented for the study of crystallization kinetics of liquid crystal mesogens.
2. In tilted ordering (smectic  $F^*$  phase) the formation of an ordered domains occurs which converts to a stable nucleus that initiates the aggregation of the surrounding molecules to form layered domains. The origin of this nucleus is critical since its formation proceeds until it reaches a sufficient size to initiate the crystallization process.
3. We propose that this process of crystallization is controlled by either the lamellar or inter layer distances in tilted (Smectic  $F^*$ ) kineto phase. In such a process of seed nucleation, factors relating to the smectic layer plays an important role. A particular molecule in the lower smectic layer first acquires the requisite energy to allow the formation of ordered domains, which in turn propagate crystallization to the adjacent smectic layers. These ordered domains will further proceed through the smectic layers by a process of successive addition of the molecules from neighboring layers leading to sporadic



nucleation and growth in two dimensions. This process continues until the crystallization is completed.

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#### REFERENCES

1. D. Demus, in *Liquid Crystals: Phase Types Structures and Chemistry of Liquid Crystals*, Springer, New York (1994).
2. M. Avrami, *J.Chem. Phy.* **7** 1103 (1939).
3. M. Avrami, *J.Chem. Phys.* **8** 212 (1940).
4. P.A. Kumar, M.L.N. Madhu Mohan, V.G.K.M. Pisipati, *Liq. Cryst.* **27** 727 (2000).
5. M.L.N. Madhu Mohan, B. Arunachalam, C.R. Aravindh Sankar, *Mat. Met. Trans. A* **39** 1192 (2008).
6. G.W. Gray, J.W. Goodby in *Smectic Liquid Crystals – Textures and Structures*, Leonard Hill, New York (1982).
7. H. Ziru, Z. Yue, C. Alain, *Liq. Cryst.* **23** 317 (1997).
8. P. Keller, B. Scheurle, *Angew Chem. Int. Ed. Engl.* **8** 884 (1969).
9. T. Chitravel, M.L.N. Madhu Mohan, V. Krishnakumar, *Mol Cryst. Liq. Cryst.* **493**, 17; (2009) *Physica B* (in press); (2009) *Z. Natur. Forch* (2008).