

# Research on the Electrical and Thermodynamical Properties of the Twisted Grain Boundary Phases of the Homologous Series of 4-*n*-alkyloxy-4'-(cholesteryloxycarbonyl-1-butyloxy) chalcone

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The present research article deals with the comparative thermodynamical and electrical studies of the compounds 4-*n*-decyloxy-4'-(cholesteryloxycarbonyl-1-butyloxy) chalcone (DC-4, 10), 4-*n*-undecyloxy-4'-(cholesteryloxycarbonyl-1-butyloxy) chalcone (DC-4, 11) and 4-*n*-dodecyloxy-4'-(cholesteryloxycarbonyl-1-butyloxy) chalcone (DC-4, 12) in order to generalize the electrical (mainly dielectric anisotropy, experimental slopes of inverse of dielectric strength with temperature and rotational viscosity) behaviors of the Twisted Grain Boundary (TGB) phases. The research article also explores the effect of the increase in the length of the alkyl chains on the dielectric properties of the above studied compounds.

A series of the nonsymmetrical liquid crystal (LC) dimers derived from cholesterol have been synthesized by Yelamagad and co-workers at Centre for Soft Matter Research, Bangalore, India [1]. They have reported independent occurrence of the twisted grain boundary (TGB) phases. The homologous series of 4-*n*-alkyloxy-4'-(cholesteryloxycarbonyl-1-butyloxy) chalcone (with tail length = 10, 11, 12) demonstrate exceptionally wide temperature range TGBA (~ 15-19 °C) and TGBC\* (~ 23-33 °C) [1, 2].

**CHEMICAL STRUCTURE AND THERMODYNAMIC STUDY OF THE TGB PHASES:** The general chemical structure of the investigated compounds is shown in **Figure 1**.

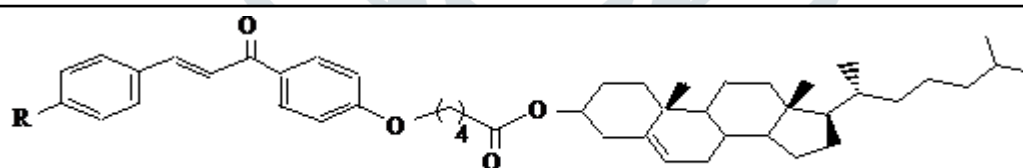


Figure 1: General molecular structure of the optically active dimeric compound, 4-*n*-alkyloxy-4'-(cholesteryloxycarbonyl-1-butyloxy) chalcone. DC-4, 10: R= OC<sub>10</sub>H<sub>21</sub>; DC-4, 11: R= OC<sub>11</sub>H<sub>23</sub>; DC-4, 12: R= OC<sub>12</sub>H<sub>25</sub>.

The peak transition temperatures ( $T_p$ ) and enthalpies ( $\Delta H$ ) corresponding to various transitions are given in **Table 1**. Differential scanning calorimeter (DSC) study in the heating and cooling cycles at the scanning rate of 5 °C/minute have been done for all homologous members of the series, namely DC-4, 10; DC-4, 11 and DC-4, 12. The DSC thermogram of the compounds DC-4, 11 and DC-4, 12 in the heating and cooling cycles are shown in **Figures 2 and 3** respectively, as representative cases.

Table 1: Transition temperature and transition enthalpy for various transitions deduced from the Differential scanning calorimeter studies for the homologous members DC-4, 10; DC-4, 11 and DC-4, 12. × demonstrates that the phase transition does not exist.

Phase Transitions	DC 4-10		DC 4-11		DC 4-12	
	T <sub>P</sub> (°C)	ΔH (J/g)	T <sub>P</sub> (°C)	ΔH (J/g)	T <sub>P</sub> (°C)	ΔH (J/g)
<i>Heating cycle</i>						
Cr <sub>1</sub> -Cr <sub>2</sub>	×	×	108.1	44.4	×	×
Cr <sub>1</sub> /Cr <sub>2</sub> -TGBA	112.7	46.2	113.9	31.5	114.3	49.4
TGBA-I	124.4	6.8	124.5	8.9	124.9	8.7
<i>Cooling cycle</i>						
I-TGBA	119.7	-6.8	121.0	-9.2	121.2	-8.3
TGBA-TGBC*	×	×	105.0	-0.17	106.7	-0.14
TGBC*-Cr	84.5	-27.9	79.3	-26.2	74.2	-28.2

The transition from TGBA to the TGBC\* phase is very weak and it could not be observed due to smearing of the transition peaks at high and low scanning rates. But after careful optimization of the scanning rate and proper magnification of the cooling thermogram, it could be possible to detect it at the scan rate of 5 °C/minute and estimate the enthalpy of the TGBA-TGBC\* transition, suggesting that it is a weak first-order transition. Primarily TGBA-TGBC\* transition was detected only under the polarized light microscope (PLM) and therefore it was suspected to be second order.

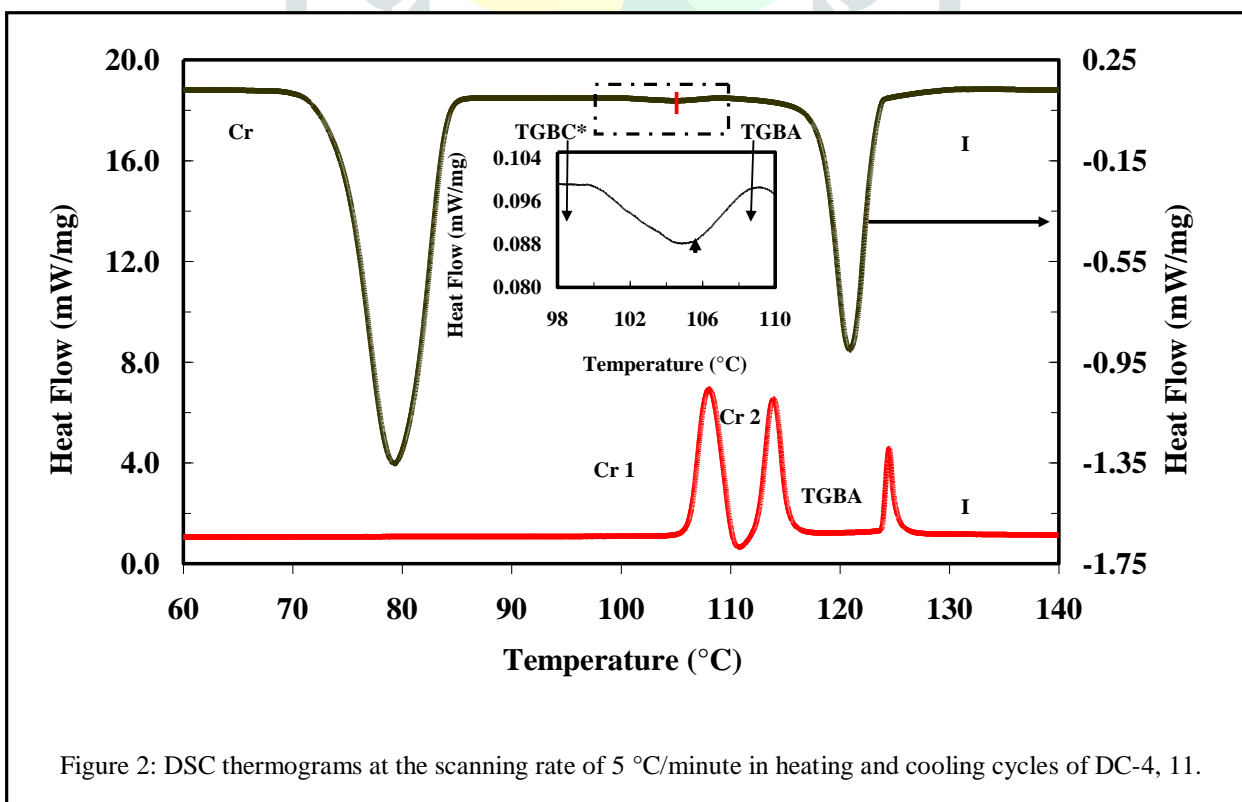


Figure 2: DSC thermograms at the scanning rate of 5 °C/minute in heating and cooling cycles of DC-4, 11.

For this weak peak, uncertainty in the determination of the peak transition temperatures is quite large and there has been no regular dependence of the peak transition temperatures on the scanning rates. The similar observations have also been reported in literature for TGB systems [3, 4]. It is important to note that most of the TGB-TGB transitions have been predicted to be second order [5, 6] but experimentally they have been found to be weakly first order transitions with transition width of the order of 0.2 to 0.5 °C in extremely pure materials as well as in the mixtures [7-9].

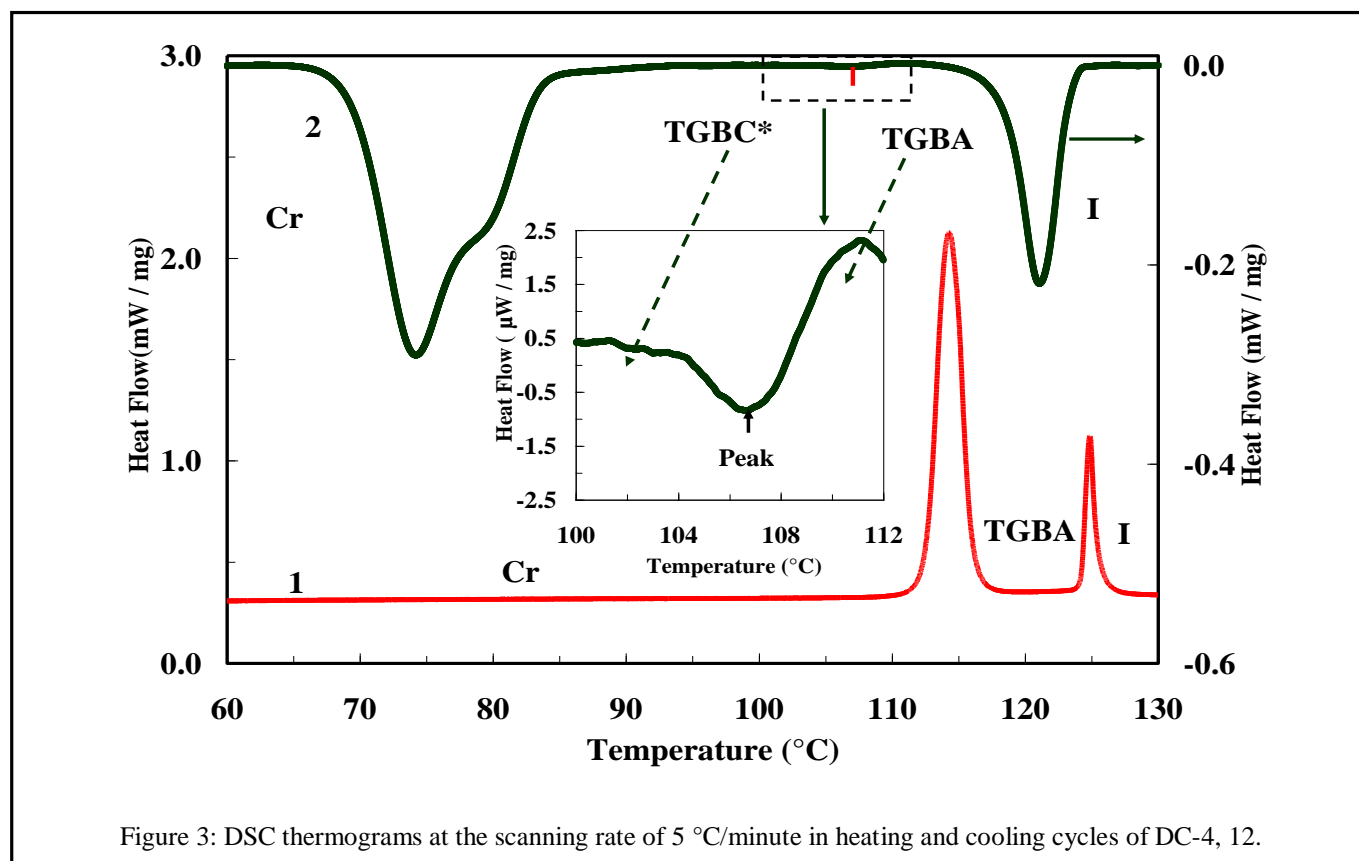
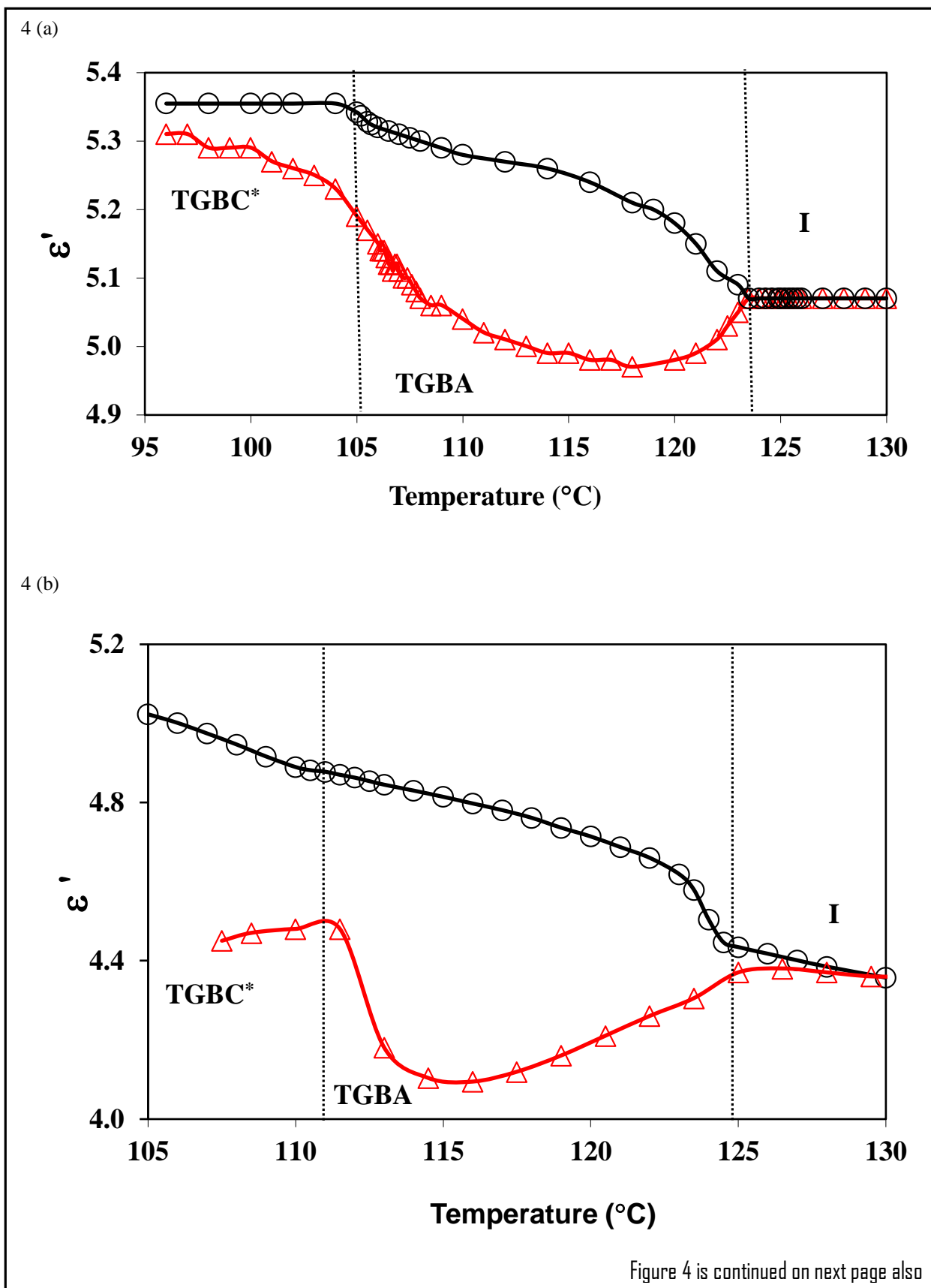
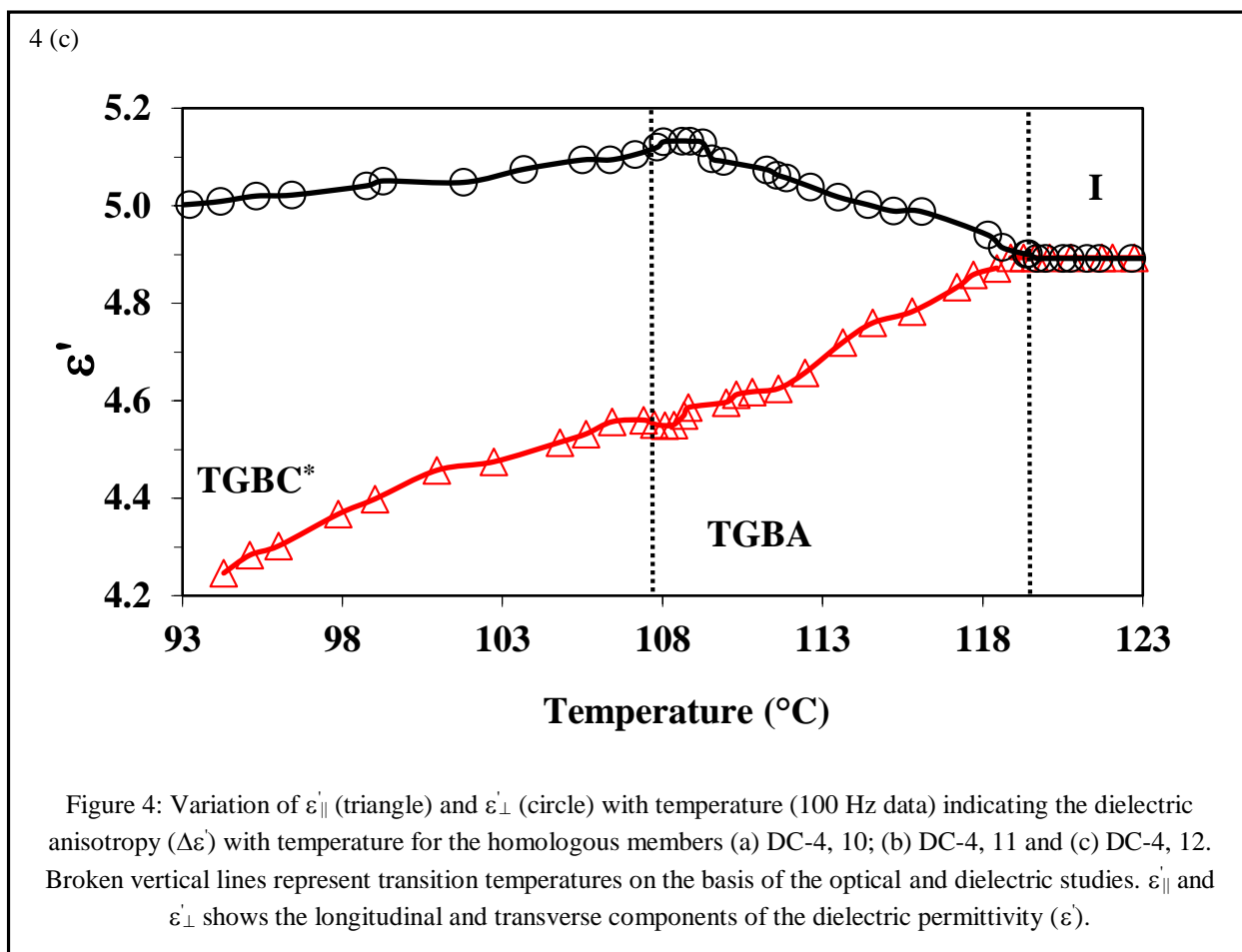


Figure 3: DSC thermograms at the scanning rate of 5 °C/minute in heating and cooling cycles of DC-4, 12.

**DIELECTRIC ANISOTROPY OF THE TGBA AND TGBC\* PHASES:** Variations of the transverse ( $\epsilon'_{\perp}$ ) and the longitudinal ( $\epsilon'_{\parallel}$ ) components of the dielectric permittivity ( $\epsilon'$ ) at 100 Hz indicating variation of the dielectric anisotropy ( $\Delta\epsilon' = \epsilon'_{\parallel} - \epsilon'_{\perp}$ ) with the temperature of the studied compounds are shown in **Figure 4**. In the case of the homeotropic aligned TGB phases, all the molecules are not orthogonal to the electrode surfaces and therefore, it may be more illustrative to express measured permittivity data in the terms of the TGB helix axis. When TGB helix axis is taken as reference axis then  $\epsilon'_{\perp}$  becomes  $\epsilon'_{\parallel h}$ , i.e. the permittivity measured along TGB helix axis. Similarly,  $\epsilon'_{\parallel}$  becomes  $\epsilon'_{\perp h}$ , i.e. the permittivity normal to TGB helix axis [10]. As expected, in the isotropic liquid phase (I)  $\Delta\epsilon'$  has been found to be  $\sim 0$  showing that there is no preferred alignment of the molecules.





Below isotropic liquid to TGBA transition temperature ( $T_{I-TGBA}$ ),  $\epsilon'_{\perp}$  increases whereas  $\epsilon'_{\parallel}$  decreases sharply with decrease in the temperature, showing negative dielectric anisotropy  $\Delta\epsilon' (= \epsilon'_{\parallel} - \epsilon'_{\perp}) < 0$  in the TGBA phase. Good planar alignment has not been achieved immediately below  $T_{I-TGBA}$ , but as the temperature decreases in TGBA phase, molecular alignment improves and that is why,  $\epsilon'_{\perp}$  increases quickly in the vicinity of the isotropic liquid to TGBA transition. After the perfect planar alignment, rate of the increase of  $\epsilon'_{\perp}$  becomes slow, however, increasing trend continues throughout the TGBA phase. On lowering the temperature, a change in the slope of  $\epsilon'_{\perp}$  data has been observed for all members of the homologous series. This suggests macroscopic change in the structure of the materials and confirms the existence of another phase below TGBA phase which has also been observed during the DSC and PLM studies. As mentioned earlier, observed square grid texture [9-21] for the homogeneously (planar) aligned materials confirms this phase as TGBC\*. At TGBA-TGBC\* transition,  $\epsilon'_{\parallel}$  increases rapidly by appreciable magnitude in the case of the first two members of the series (DC-4, 10 and DC-4, 11) and  $\epsilon'_{\parallel}$  becomes constant at lower temperatures of the TGBC\* phase. Such behaviour has been observed in some other similar systems also [22-24]. However, in the case of DC-4, 12 [25],  $\epsilon'_{\parallel}$  decreases continuously with decrease in the temperature throughout TGBC\* phase [Figure 4 (c)]. However, it is emphasized that TGB in general and TGBC\* structure in particular are complex one and thus  $\Delta\epsilon'$  shown in Figure 4 is not directly representing dielectric anisotropy as defined for the simplest nematic and orthogonal smectics [26-44].

**EXPERIMENTAL SLOPES OF THE INVERSE OF DIELECTRIC STRENGTH WITH TEMPERATURE AND ROTATIONAL VISCOSITY:** The soft mode like relaxations in both TGBA and TGBC\* phases for the planar alignment of the materials have been reported [2, 25]. It has been further observed that the variation of the inverse of the dielectric strength ( $\delta\epsilon^{-1}$ ) of the soft mode like relaxation with temperature is linear except for the immediate vicinity of the transition temperatures in both TGB (A and C\*) phases.

Table 2: Dielectric strength slopes ( $d\delta\epsilon_s^{-1}/dT$  in  $^{\circ}\text{C}^{-1}$ ) in planar anchoring of the molecules for all members of the series.

Name of the series compound	$\left(\frac{d\delta\epsilon_s^{-1}}{dT}\right)_{\text{TGBA}}$	$\left(\frac{d\delta\epsilon_s^{-1}}{dT}\right)_{\text{TGBC}^*}$
DC-4, 10	0.053	0.049
DC-4, 11	2.350	0.570
DC-4, 12	0.039	0.007

It has been calculated that the slopes of the inverse of the dielectric strength with temperature of TGBC\* phase is less than that of the TGBA phase for all the homologous members DC-4, 10; DC-4, 11 and DC-4, 12 (see **Table 2**). For the relative study of the rotational viscosity in planar anchoring of the molecules for TGBA and TGBC\* phases, the theoretical expressions from Ismaili et al. [45] (see **Equations 1 and 2**) have been used.

$$(\delta\epsilon_s \times f_R)_{\text{TGBA}} = \frac{\epsilon_0 \chi^2 C^2}{2\pi\gamma_{\text{TGBA}}} \quad (1)$$

$$(\delta\epsilon_s \times f_R)_{\text{TGBC}^*} = \frac{\epsilon_0 \chi^2 C^2}{2\pi\gamma_{\text{TGBC}^*}} \cos^2(\theta_s) \quad (2)$$

where  $\gamma_{\text{TGBA}}$  and  $\gamma_{\text{TGBC}^*}$  are viscosity of the soft mode like relaxation of TGBA and TGBC\* phases. One can note that  $\cos^2(\theta_s)$  is the result of the two projections: projection of the applied field say  $E_x$  on the smectic planes and projection on the X-direction of the dipoles induced in the smectic planes. This geometric factor is almost equal to unity, since the spontaneous tilt angle is rarely higher than  $15^{\circ}$  in the TGBC\* phase [45]. The plots of  $\delta\epsilon_s \times f_R$  versus temperature are shown in **Figure 5**, shows that the product  $\delta\epsilon_s \times f_R$  have higher value in TGBA than in the TGBC\* phase for all members of the series. Consequently rotational viscosity ( $\gamma$ ) is expected to be lower in TGBA than in the TGBC\* phase. As, previously, it has been reported [2, 25]; that the activation energy of the TGBA phase is less and relaxation frequency is higher than that of the TGBC\* phase, the phenomenon confirms that viscosity is lower in TGBA than TGBC\* phase. The variation of  $|\Delta\epsilon|$  with number of the alkyl chains ( $n$ ) present in each member of the series is shown in **Figure 6**. The linear equation for TGBA and TGBC\* phases have been established as illustrated below.

For TGBA phase:  $\Delta\epsilon' = 0.225 n - 2.1917$  (3)

For TGBC\* phase:  $\Delta\epsilon' = 0.225 n - 1.9933$  (4)

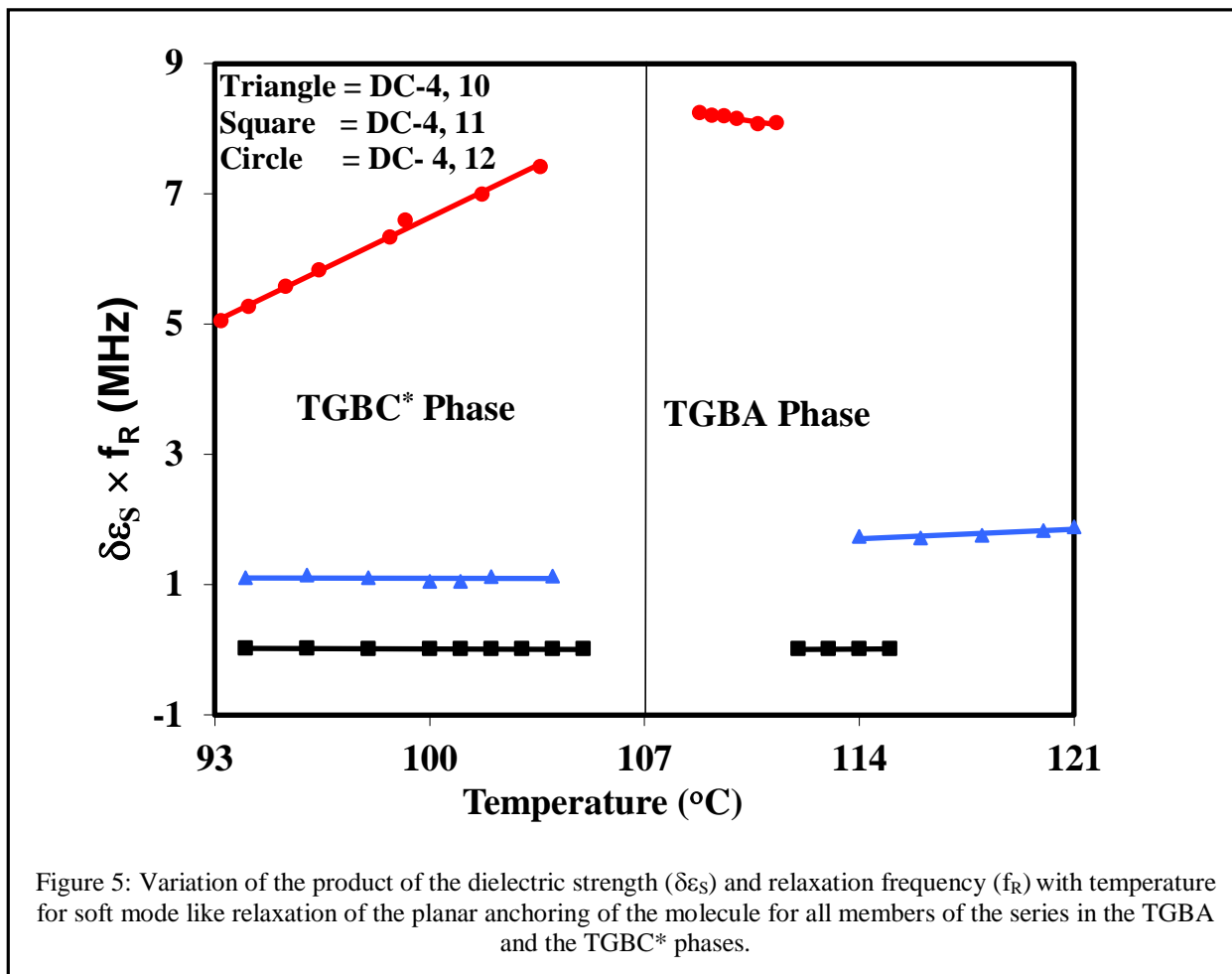


Figure 5: Variation of the product of the dielectric strength ( $\delta\epsilon_s$ ) and relaxation frequency ( $f_R$ ) with temperature for soft mode like relaxation of the planar anchoring of the molecule for all members of the series in the TGBA and the TGBC\* phases.

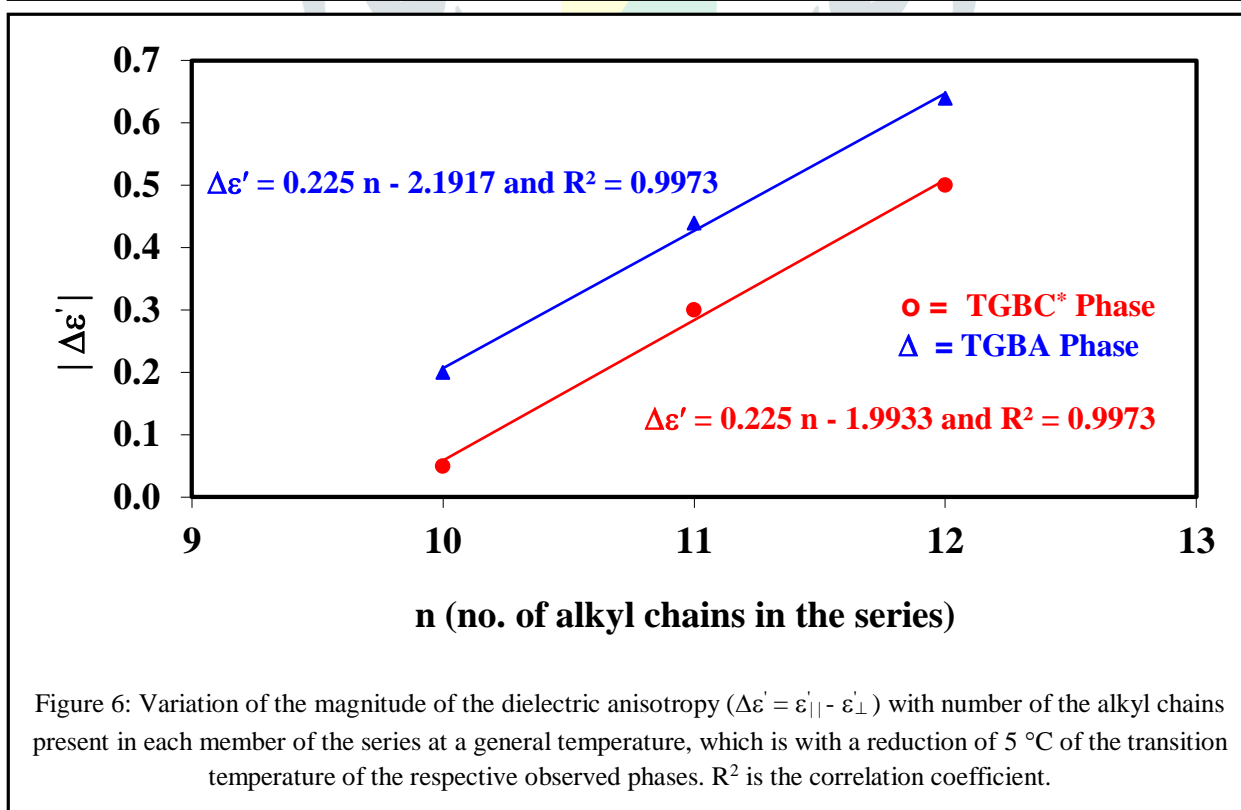


Figure 6: Variation of the magnitude of the dielectric anisotropy ( $\Delta\epsilon' = \epsilon'_{||} - \epsilon'_{\perp}$ ) with number of the alkyl chains present in each member of the series at a general temperature, which is with a reduction of 5 °C of the transition temperature of the respective observed phases.  $R^2$  is the correlation coefficient.

From **Equations (3)** and **(4)**, it has been noticed that, the value of the slope of the lines in the TGBA and TGBC\* phases are equal ( $\sim 0.225$ ), i.e. both the line indicates same steepness. Also, it has been noticed that, the value of the correlation coefficient ( $R^2$ ) in the TGBA and TGBC\* phases are equal ( $\sim 0.9973$ ). It suggests that, the tendency of the both the lines resemble to each other (see **Figure 6**). Due to the elongation of the chain length, magnitude of the dielectric anisotropy ( $|\Delta\epsilon'|$ ) increased as in the nematic case [46] and the same is evident from **Figure 6**.

**CONCLUSIONS:** Following points summarize the comparative experimental results of the homologous series of 4-*n*-alkyloxy-4'-(cholesteryloxycarbonyl-1-butyloxy) chalcone (with tail length = 10, 11 and 12):

- The extensive thermodynamical and electrical studies support the existence of the wide temperature range TGBA and TGBC\* phases.
- Thermodynamical study suggests that TGBA-TGBC\* transition is weakly first order.
- Dielectric anisotropy ( $\Delta\epsilon'$ ) has been found to be negative in TGBA and TGBC\* phases for all studied members of the series. Dielectric anisotropy decreases in TGBC\* phases for the 10<sup>th</sup> and 11<sup>th</sup> member and increases for the 12<sup>th</sup> member.
- It has been found that, with the exception of the near neighborhood of the transition temperatures, the variation of the inverse of the dielectric strength with temperature is linear in both the TGB phases. Slope of the TGBC\* phase is less than that of the TGBA phase for all members of the compound.
- For the soft mode like relaxations, the product of the dielectric strength and relaxation frequency is higher in TGBA than in TGBC\* phase, accordingly the rotational viscosity is expected to lower in the TGBA than in the TGBC\* phase.
- In the variation of the dielectric anisotropy with number of the alkyl chains present in each member of the series, it has been established that, the slope of the line for TGBA and TGBC\* phases indicates same steepness and also the tendency of the both lines are resemble to each other.
- Due to the elongation of the chain length, magnitude of the dielectric anisotropy ( $|\Delta\epsilon'|$ ) increased.

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