

Twisted Grain Boundary Phases of the Homologous Series of 4-*n*-alkyloxy-4'-(cholesteryloxycarbonyl-1-butyloxy) chalcone: A Comparative Analysis with Implications for the Future

Prashant Kumar Pandey

Associate Professor (Applied Physics), Department of Applied Sciences, Ansal Technical Campus, Sector-C, Pocket-9, Sushant Golf City, Lucknow (India).

Thermodynamical, optical and dielectric properties of the twisted grain boundary (TGB) phases of optically active nonsymmetrical liquid crystalline dimeric compounds 4-*n*-alkyloxy-4'-(cholesteryloxycarbonyl-1-butyloxy) chalcone (with tail length = 10, 11, 12) showing exceptionally wide temperature range TGBA (~ 15-19 °C) and TGBC* (~ 23-33 °C) phases have been carried out by the differential scanning calorimeter (DSC), polarized light microscopy (PLM) and impedance spectroscopy.

THERMODYNAMICAL STUDIES: DSC study in the heating and cooling cycles at the scanning rate of 5 °C/minute have been carried out. The thermodynamical study in combination with optical texture study support the existence of the wide temperature range TGBA and TGBC* phases (see **Table 1**).

Table 1: Transition temperature for various transitions obtained from the Differential Scanning Calorimeter in combination with optical texture study for the studied members i.e. 10th [1], 11th [2] and 12th [3] of the homologous series of 4-*n*-alkyloxy-4'-(cholesteryloxycarbonyl-1-butyloxy) chalcone. × demonstrates that the phase transition does not exist.

Phase Transitions	10 th member	11 th member	12 th member
	T _P (°C)	T _P (°C)	T _P (°C)
<i>Heating cycle</i>			
Cr-Cr'	×	108.1	×
Cr/ Cr'-TGBA	112.7	113.9	114.3
TGBA-I	124.4	124.5	124.9
<i>Cooling cycle</i>			
I-TGBA	119.7	121.0	121.2
TGBA-TGBC*	×	105.0	106.7
TGBC*-Cr	84.5	79.3	74.2

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.

OPTICAL STUDIES: The square grid pattern texture has been observed for low temperature phase (i.e. TGBC*) under crossed polarizing microscope having magnification of 100X when slides are treated for the

planar anchoring conditions of the molecular director. A typical characteristic pattern for the TGBA and TGBC* phase is the filament texture which has been observed for the studied compound, for the homeotropic anchoring conditions of the molecular director. The filaments observed in the TGBC* phase are different from those the TGBA phase. The TGBC* filaments are undulatory in nature, the period of undulation being about the same as that of the square grid pattern obtained in the planar geometry.

DIELECTRIC STUDIES: Planar oriented molecules show a soft mode like relaxation due to the tilt fluctuation of molecules in the frequency range of ~ 40 kHz to 8 MHz in both the TGB (A and C*) phases for all studied members i.e. 10th [1], 11th [2] and 12th [3] of the homologous series of 4-*n*-alkyloxy-4'-(cholesteryloxy-carbonyl-1-butyloxy) chalcone (see **Table 2**). It is important to mention here that $\delta\epsilon$ of the soft mode like relaxation of the TGBA phase of some other molecular systems is of the same order [4]. It is apparent from the dielectric data that the relaxation mode of the TGBA phase continues in the TGBC* phase as well, with increase in its strength (see **Table 2**). However, this strength is not yet sufficient to show a detectable loss peak in the presence of the high-frequency parasitic effect [5, 6] at about 1- 8 MHz in the loss data. From the dielectric data, it is also clear that, range of the relaxation frequency (f_R) i.e. ~ 40 -7700 kHz for the observed mode (presumably the soft mode) of TGBA/TGBC* phase is larger than the range of f_R i.e. ~ 5 -800 kHz for the soft mode of SmA* and SmC* phases of ferroelectric systems [7-36]. This is due to the presence of the elastic parameter H_2 (of TGB phases) in the numerator of **Equation (1)**. Similarly, presence of H_2 in the denominator of **Equation (2)** reduces dielectric strengths (~0.1-1.5) of the soft mode ($\delta\epsilon_S$) of these TGB phases as compared to $\delta\epsilon_S$ (~1-300) of the SmA* and SmC* phases of the ferroelectric systems [7-36].

$$f_s = \frac{\alpha(T - T_C) + H_2}{2\pi\gamma_s} \quad (1)$$

$$\delta\epsilon_S = \frac{\epsilon_0 \chi_e^2 C^2}{\alpha(T - T_C) + H_2} \quad (2)$$

$$\epsilon^* = \epsilon' - j\epsilon'' = \epsilon(\infty) + \sum_i \frac{(\delta\epsilon)_i}{1 + (j\omega\tau_i)^{1-h_i}} + \frac{A}{\omega^n} - j \frac{\sigma_{ion}}{\epsilon_0 \omega^k} - jBf^m \quad (3)$$

$$f_G = \frac{H_2}{2\pi\gamma_G} \quad (4)$$

For the planar anchoring condition of the molecules, in the low-frequency region (<1 kHz) of the TGBC* phase, ϵ'_\perp increases upon decreasing the temperature. The value of ϵ'_\perp increases upon cooling in the frequency range of 1 kHz to 10 Hz. This indicates the presence of another collective relaxation mechanism in this phase between 1 kHz to 10 Hz. However, data below 100 Hz are affected due to low-frequency parasitic contributions [37]. To

explore the behaviour of the expected low frequency mode, dielectric dispersion curves have been fitted with **Equation (3)**. After subtracting electrode polarization effects, low frequency mode is clearly visible in the TGBC* phase. On the basis of the dielectric data, it has been established that this relaxation mode is analogous to the Goldstone mode of SmC* phase of the ferroelectric systems. Although theoretical modelling for the Goldstone mode of TGBC* is yet to be done, but on the basis of the analogy of the TGBC phase one may conclude that low values of the relaxation frequencies (of the Goldstone like mode of TGBC* phase) may be due to the low value of the anchoring strength and high viscosity (see **Equation 4**) of the TGBC* phase of the present molecular systems. The small value of the transverse component of the molecular dipole moment may be another reason for the weak Goldstone mode [38].

Table: 2 Relaxation frequency (f_R in kHz), dielectric strength ($\delta\epsilon$), slope of the inverse of the dielectric strength with temperature ($d\delta\epsilon^{-1}/dT$ in $^{\circ}C^{-1}$) and activation energy (W_a in kJ/mole) for the soft mode like relaxation due to the tilt fluctuation of the molecules in the TGB (A and C*) phases for all studied members i.e. 10th [1], 11th [2] and 12th [3] of the homologous series of 4-*n*-alkyloxy-4'-(cholesteryloxycarbonyl-1-butyloxy) chalcone.

Members	(f_R) _A	(f_R) _{C*}	($\delta\epsilon$) _A	($\delta\epsilon$) _{C*}	($d\delta\epsilon^{-1}/dT$) _A	($d\delta\epsilon^{-1}/dT$) _{C*}	(W_a) _A	(W_a) _{C*}
10 th	~2500-3500	~1000-2200	0.54-0.68	0.73-1.1	0.48	0.43	45.5	56.3
11 th	~100-160	~40-80	0.102-0.108	0.11-0.47	2.35	0.56	30.9	37.3
12 th	~7100-7700	~3700-6000	1.03-1.14	1.23-1.36	0.04	0.008	34.2	38.4

Table: 3 Relaxation frequency (f_R in Hz) and dielectric strength ($\delta\epsilon$) of the Goldstone mode like relaxation due to the phase fluctuation of the molecules in the TGBC* phase for the studied members 10th [1], 11th [2] and 12th of the homologous series of 4-*n*-alkyloxy-4'-(cholesteryloxycarbonyl-1-butyloxy) chalcone. × demonstrates that the mode could not be observed.

Members	(f_R) _{TGBC*}	($\delta\epsilon$) _{TGBC*}
10 th	~ 200-300	~ 0.20-0.30
11 th	~ 40-250	~ 0.10-0.80
12 th	×	×

In the homeotropic anchoring of molecules, the measured the dielectric permittivity (ϵ') in the isotropic liquid phase to TGBC* phase is almost invariant in the frequency range of 1 Hz to 10 MHz for 10th and 11th members implying that no dipolar relaxation phenomenon in this frequency range. However, for the 12th member, a relaxation mechanism occurs on higher frequency side in the TGBA and TGBC* phases. The dielectric strength and relaxation frequency of the observed mode has been found to be in the ranges of ~0.4-0.7 and ~3.2-5.4 MHz

respectively. The nature of the molecular alignment (homeotropic), the Cole-Cole fitting of the dielectric data, temperature dependence of relaxation frequency, and magnitude of activations energies in various mesophases suggest that this mode arises due to the rotation of individual molecules about their short axes [3, 4]. For 10th and 11th members of the series, relaxation frequencies seems beyond 10 MHz due to small molecular length (as compared to 12th member) and hence could not be detected due to experimental limitations. 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. (see **Equations 5** and **6**) have been used.

$$(\delta\varepsilon_s \times f_R)_{\text{TGBA}} = \frac{\varepsilon_0 \chi^2 C^2}{2\pi\gamma_{\text{TGBA}}} \quad (5)$$

$$(\delta\varepsilon_s \times f_R)_{\text{TGBC}^*} = \frac{\varepsilon_0 \chi^2 C^2}{2\pi\gamma_{\text{TGBC}^*}} \cos^2(\theta_s) \quad (6)$$

The plots of $\delta\varepsilon_s \times f_R$ versus temperature shows that the product $\delta\varepsilon_s \times f_R$ have higher value in TGBA than in the TGBC* phase for all members of the series. Consequently rotational viscosity (γ) is expected to be lower in TGBA than in the TGBC* phase. As the activation energy of the relaxation process for the TGBA phase is less and relaxation frequency is higher than that of the TGBC* phase (see **Table 2**), the phenomenon confirms that viscosity is lower in TGBA than in TGBC* phase. Dielectric anisotropy ($\Delta\varepsilon' = \varepsilon'_{\parallel} - \varepsilon'_{\perp}$) has been found to be negative (< 0) in TGBA and TGBC* phases for all studied members of the series (see **Table 4**).

Table: 4 The variation of ($\Delta\varepsilon' = \varepsilon'_{\parallel} - \varepsilon'_{\perp}$) with number of the alkyl chains (n) present in each member of the series for the TGB (A and C*) phases.

n	10	11	12
($\Delta\varepsilon'$) _A	-0.20	-0.44	-0.64
($\Delta\varepsilon'$) _{C*}	-0.05	-0.30	-0.50

The variation of $\Delta\varepsilon'$ with number of the alkyl chains (n) present in each member of the series gave the linear variation for TGBA and TGBC* phases. From, these variations, it has been noticed that, the value of the slope of the lines in the TGBA and TGBC* phases are equal (0.225), i.e. both the lines indicate same steepness. Also, it has been noticed that, the value of the correlation coefficient (R^2) in the TGBA and TGBC* phases are equal (0.9973). It suggests that, the tendency of the both the lines resemble to each other. Due to the elongation of the chain length, magnitude of the dielectric anisotropy ($|\Delta\varepsilon'|$) increased as in the nematic case [39] and the same is evident from **Table 4**.

FUTURE PROSPECTS: The TGB phases of liquid crystals (LCs) are characterized not only by bulk properties viz. weak transition enthalpy, optical texture, dielectric permittivity, dielectric anisotropy and viscosity etc. but also from the molecular parameters (relaxation frequency, dielectric strength etc.) for their mutual association and rotation under an applied electric field. Dielectric relaxation phenomenon of TGB phases of LCs are related to the response of LC molecules to the application of an electric field. Therefore, studies of the above parameters are important to understand the molecular dynamics and fundamental properties of TGB phases vis-à-vis molecular design. In the present study, various dielectric relaxation modes in the wide temperature range of TGBA and TGBC* phases have been detected. However, due to their weak dielectric strength, precise quantitative analysis could not be possible. In future, the synthesis of a molecular system with large value of the transverse component of the dipole moment may yield independent clear characteristics of these modes. Thermodynamic, optical and dielectric studies of the TGB phases gave temperature range, stability of the TGB phases, optical textures, frequency and temperature dependent dielectric parameters for the studied materials. It has been able to correlate studied parameters with the existing theoretical formulations. Future scope in the field is to generalize the above formulations based on the studied parameters for large number of systems to build up a fundamental physics/new theory regarding TGB phases of LC materials. It may also be important to see whether TGB phases have technological importance like those of blue phases [40-49] which are another kind of frustrated phases.

REFERENCES:

- [1] Pandey, A.S.; Dhar, R.; Pandey, M.B.; Achalkumar, A.S.; Yelamaggad, C.V. *Liq. Cryst.* 2009, **36**, 13.
- [2] Pandey, A.S.; Dhar, R.; Achalkumar, A.S.; Yelamaggad, C.V. *Liq. Cryst.* 2011, **38**, 775.
- [3] Pandey, A.S.; Dhar, R.; Achalkumar, A.S.; Yelamaggad, C.V. *Bentham Open Crystallography Journal* 2011, **4**, 49.
- [4] Gupta, M.; Dhar, R.; Agrawal, V.K.; Dabrowski, R.; Tykarska, M. *Phys. Rev. E* 2005, **72**, 021703-1-10.
- [5] Srivastava, S.L. *Proc. Natl. Acad. Sci. India* 1993, **63**, 311.
- [6] Dhar, R. *Indian J. Pure Appl. Phys.* 2004, **42**, 56.
- [7] Pandey, M.B.; Dhar, R.; Agrawal, V.K.; Dabrowski, R.; Tykarska, M. *Liq. Cryst.* 2004, **31**, 973.
- [8] Novotna, V.; Hamplova, V.; Kaspar, M.; Podoliak, P.; Bubnov, A.; Glogarova, M.; Nonnenmacher, D.; Giesselmann, F. *Liq. Cryst.* 2011, **38**, 649.
- [9] Stojanovic, M.; Bubnov, A.; Obadovic, D.Z.; Hamplova, V.; Kaspar, M.; Cvetinov, M. *Phase Transitions* 2011, **84**, 380.
- [10] Piecek, W.; Bubnov, A.; Perkowski, P.; Morawiaka, P.; Ogrodnika, K.; Rejmerc, W.; Zurowska, M.; Hamplova, V.; Kaspar, M. *Phase Transitions* 2010, **83**, 551.
- [11] Podoliak, N.; Novotna, V.; Glogarova, M.; Hamplova, V.; Kaspar, M.; Bubnov, A.; Kapernaum, N.; Giesselmann, F. *Phase Transitions* 2010, **83**, 1026.
- [12] Bubnov, A.; Domenici, V.; Hamplova, V.; Kaspar, M.; Veracini, C. A.; Glogarov, M. *J. Phys. Condens. Matter* 2009, **21**, 035102.

- [13] Malik, P.; Raina, K. K.; Bubnov, A.; Prakash, C. *Phase Transitions* 2006, 79, 889.
- [14] Bubnov, A.; Kaspar, M.; Hamplova, V.; Glogarova, M.; Samaritani, S.; Galli, G.; Andersson, G.; Komitov, L. *Liq. Cryst.* 2006, 33, 559.
- [15] Kaspar, M.; Bubnov, A.; Hamplova, V.; Pirkl, S.; Glogarova, M. *Liq. Cryst.* 2004, 31, 821.
- [16] Novotna, V.; Hamplova, V.; Kaspar, M.; Glogarova, M.; Bubnov, A.; Lhotakova, Y. *Ferroelectrics* 2004, 309, 103.
- [17] Hamplova, V.; Bubnov, A.; Kaspar, M.; Novotna, V.; Pociecha, D.; Glogarov, M. *Liq. Cryst.* 2003, 30, 627.
- [18] Bubnov, A.; Pakhomov, S.; Kaspar, M.; Hamplova, V.; Glogarova, M. *Mol. Cryst. Liq. Cryst.* 1999, 328, 317.
- [19] Gupta, S. K.; Singh, D.P.; Manohar, R.; Hiremath, U.S.; Yelmaggad, C.V. *Liq. Cryst.* 2012, 39, 1125.
- [20] Pandey, M.B.; Dhar, R.; Dabrowski, R.; *Mol. Cryst. Liq. Cryst.*, 2011, 541, 222.
- [21] Dwivedi, A.; Dhar, R.; Pandey, M.B.; Das, I.M.L.; Dabrowski, R. *Journal of Molecular Liquids* 2009, 148, 1.
- [22] Song, J.K.; Manna, U.; Fukuda, A.; Vij, J.K. *Applied Physics Letters*. 2008, 93, 142903.
- [23] Rutkowska, J.; Perkowski, P.; Raszewski, Z.; Kedzierski, J. *Opto-Electron. Rev.* 2008, 16, 262.
- [24] Perkowski, P.; Ogrodnik, K.; Lada, D.; Piecek, W.; Rutkowska, J.; Raszewski, Z.; Zurowska, M.; Dabrowski, R.; Sun, X. *Opto-Electron. Rev.* 2008, 16, 277.
- [25] Choudhary, A.; Kaur, S.; Prakash, J.; Sreenivas, K.; Bawa, S.S.; Biradar, A.M. *Jour. of Appl. Phys.* 2008, 104, 034105.
- [26] Manna, U.; Song, J.K.; Panarin, P.Y.; Fukuda, A.; Vij, K.J. *Phys. Rev. E* 2008, 77, 041707.
- [27] Kutnjak, Z. *Ferroelectrics* 2008, 369, 133.
- [28] Kaspar, M.; Novotna, V.; Hamplova, V.; Pociecha, D.; Glogarova, M. *Liq. Cryst.* 2008, 35, 975.
- [29] Goel, P.; Singh, G.; Pant, P.B.; Biradar, A.M. *Liq. Cryst.* 2012, 39, 927.
- [30] Marino, L.; Bruno, E.; Desanto, M.P.; Ciuchi, F.; Marino, S.; Scaramuzza, N. *Mol. Cryst. Liq. Cryst.* 2012, 558, 120.
- [31] Guo, L.; Gorecka, E.; Pociecha, D.; Vaupoti, N.; Cepic, M.; Reddy, R.A.; Gornik, K.; Araoka, F.; Clark, N.A.; Walba, D.M.; Ishikawa, K.; Takezoe, H. *Physical Review E* 2011, 84, 031706.
- [32] Manohar, R.; Srivastava, A.K.; Tripathi, P.K.; Sing, P.D. *J. Mater. Sci.* 2011, 46, 5969.
- [33] Liao, C.T.; Lee, J.Y.; Lai, C.C. *Materials Chemistry and Physics* 2011, 125, 749.
- [34] Dwivedi, A.; Dhar, R.; Agrawal, V.K.; Dabrowski, R.; Ziobro, D. *Mol. Cryst. Liq. Cryst.*, 2011, 541, 262.
- [35] Nagaraj, M.; Sreenilayam, S.P.; Panarin, Y.P.; Vij, J.K.; Keith, C.; Tschierske, C. *Mol. Cryst. Liq. Cryst.*, 2011, 540, 82.
- [36] Marzec, M.; Bohdon, M.; Chrusciel, M.D.O.; Chrusciel, J.; Wrobel, S. *Mol. Cryst. Liq. Cryst.* 2011, 540, 227.
- [37] Srivastava, S.L.; Dhar, R. *Indian. J. Pure Appl. Phys.* 1991, 29, 745.

- [38] Pandey, M.B.; Dhar, R.; Agrawal, V.K.; Khare, R.P.; Dabrowski, R. *Phase Transitions* 2003, 76, 945.
- [39] Kresse, H. *Advances in Liquid Crystals*, edited by Brown, G.H. Academic Press, Inc. New York 1983, 6, 109.
- [40] Zhibing, G.; Sebastian, G.; Meizi, J. et al. *App. Phy. Lett.* 2009, 94, 101104.
- [41] Linghui, R.; Hui-Chuan, C.; Shin-Tson, W. et al. *App. Phy. Lett.* 2009, 95, 231101.
- [42] Linghui, R.; Hui-Chuan, C.; Shin-Tson, W. *J. of Disp. Tech.* 2010, 6, 287.
- [43] Yanqing, C.; Yubao, S.; Guoqiang, Y. *Liq. Cryst.* 2011, 38, 555.
- [44] Jian-Peng, C.; Feng, Z.; Qiong-Hua, W. *J. of Disp. Tech.* 2011, 7, 398.
- [45] Yan, L.; Shin-Tson, W. *J. of Disp. Tech.* 2011, 7, 359.
- [46] Jian-Peng, C.; Qiong-Hua, W. Feng, Z. *J. of the Soc. for Inform. Disp.* 2011, 19, 709.
- [47] Yoshiharu, H.; Daisuke, K.; Akio, Y. et al. *J. of the Soc. for Inform. Disp.* 2012, 20, 38.
- [48] Li-Wei, L.; Jian-Peng, C.; Da-Hai, L. et al. *J. of the Soc. for Inform. Disp.* 2012, 20, 337.
- [49] Choi, H.; Higuchi, H.; Ogawa, Y.; Kikuchi, H. *App. Phy. Lett.* 2012, 101, 131904.

