Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Padmajarani, G. , Potukuchi, D. M. and Pisipati, V. G. K. M.(1998) 'Frequency shift in smectic multiple relaxations and the effect of a flexible end chain', Liquid Crystals, 25: 5, 589 — 595

To link to this Article: DOI: 10.1080/026782998205877

URL: http://dx.doi.org/10.1080/026782998205877

LIQUID CRYSTALS, 1998, VOL. 25, NO. 5, 589–595

Frequency shift in smectic multiple relaxations and the effect of a flexible end chain

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(*Received 10 October 1997; accepted 18 May 1998*)

The low frequency (LF) dielectric constant was studied as a function of temperature in the Schiff's base liquid crystalline compounds of *N*(*p*-*n*-alkoxybenzylidene)-*p*-*n*-alkylanilines with the applied field parallel to the director to determine the phase transition temperatures and the underlying dipolar association. The low frequency (1 kHz to 10 MHz) complex dielectric spectrum systematically studied in the smectic polymorphs of these compounds implied multiple relaxations. The rotational degrees of freedom were found to be squeezed with the decrease of temperature as the low temperature smectic phases were approached. The Cole–Davidson method was used to differentiate the fast dynamics of the rigid core-associated dipole from the slow component of the flexible end chain. A comparative study of the orientational dynamics of the rigid core dipole (type I) was carried out by designing a normalized scale in smectic phases. Arrehenius dependence was used in the estimation of smectic relaxation frequency at a common normalized smectic temperature scale point. The results imply the downward shift of frequency with increase in length of the flexible end chain. The distinct loss of rotational degrees of freedom of the rigid core dipole with increasing chain length suggests its solute particle behaviour in the solvent concentration.

1. Introduction

The advent of interest in liquid crystallinity opened a new era of fundamental research [1] involving the melting of one- and two-dimensional crystals. It has also become a challenging task for the synthetic chemist for an imaginative design of the liquid crystal (LC) molecule with an improved electro-optic (EO) response, tuned through the inherent large optical anisotropy, for its use in display devices under a confined geometry. The study [2–4] of the dielectric dispersion of a material provides valuable information regarding the dipolar response (and its time regime) to the external stimulus. Recent LC dielectric research [5] attaches more importance to smectic polymorphs (rather than nematics with millisecond response times) either in their orthogonal (A*) or tilted (C*) versions with faster bistable EO response in their electro-clinic mode or in SSFLC geometry. However, an LC molecule is known [6] to possess an essentially rigid core along with flexible end chains. The associated electronic cloud is not homogeneously distributed over the length of the molecule and hence the response to external fields appears rather complex. The achiral rod-like LC molecule generally possesses [7, 8] two principal relaxations, i.e. one associated with reorientation about its long molecular axis and the other about its short axis. Though the reorientation mechanism about the long axis is rather complex, the short axis dipolar mechanism may be explained [9] by Debye's theory. It may also be pointed out that, from the Marcelja theory [10], the axial polarizabilities play a dominant role in explaining odd–even effects in the nematic and smectic physical properties of the LC compounds of a homologous series. The odd–even effect is found to be due to the *cis*- or *trans*-like alternating dipole configuration projected onto the length of the molecule with increasing end chain length. The contribution of transverse dipole moment reported [11] in high temperature glass materials and LC compounds further suggests the complex but effective role played by perpendicular dipoles in their dipolar response. A general LC molecule of *n*O.*m* type (O is the rigid core, *n* the number of alkoxy carbon atoms, *m* the number of alkyl carbon atoms) is characterized by a dipole associated with the central core (–CH=N–) and another with the flexible part, i.e. at the flexible part bridged (through electronegative oxygen) to the core. Such a distinct and differentiated dipolar response is explained [11] through the Debye mechanism. Further, the complex dielectric spectrum evidences [12] characteristic LC orientational smectic relaxations, especially in the radio frequency range. Hence, it is very useful to study the dielectric response of the rigid core and the effect of increasing

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the flexible end chain length (by keeping the core unaltered) through systematic studies such as by varying *n* and *m* in the *n*O.*m* molecule.

The presented systematic study and subsequent analysis have been carried out on the observed temperature dependence of the complex dielectric dispersion in Schiff's base *n*O.*m* compounds in their smectic A, C, F, B_{cryst}, F and G phases (smectic B and G known as soft crystals), over the frequency range of 1 kHz to 13 MHz. The compounds studied were:

N-(*p*-*n*-octyloxybenzylidene)-*p*-*n*-alkylanilines, viz. 8O.*m* with $m = 6$ and 7;

N-(*p*-*n*-nonyloxybenzylidene)-*p*-*n*-alkylanilines, viz. 9O.*m* with $m = 6$;

N-(*p*-*n*-decyloxybenzylidene)-*p*-*n*-alkylanilines, viz. 10O.*m* with $m = 8$ [12], 9 and 10.

These higher homologues of *n*O.*m* compounds were selected for the systematic study of the relaxation trend as higher homologues are known to introduce more orientational disorder than their lower counterparts. Further, the proposed study on increasing the flexible end chain can be realized in two ways, i.e. either by varying the length of the alkoxy chain (in the *n*O.6 series for $n = 8$ and 9) or by variation of the alkyl chain (in the 10O.*m* series for $m = 8$, 9 and 10).

This paper is presented in four sections: § 1 describes the state and relevance of the problem undertaken; § 2 discusses the application of theory to the analysis of the experimental observations; § 3 gives experimental details of the instruments used, preparation of cells, calibration, lead capacitance, temperature control, etc.; § 4 gives the systematic procedure followed to separate out the true LC relaxations from ionic impurity and conductive coating contributions in the dielectric spectrum. Section 4 further details the necessity of the normalization of temperature to evolve a common and universal temperature scale for comparison of smectic LC dipolar responses.

2. Theory

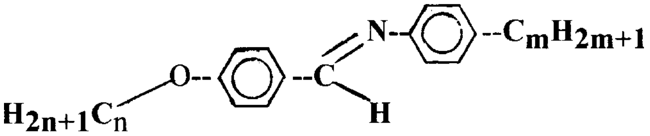
The observed complex dielectric spectrum involving orientational relaxations can be studied through the Maier–Saupe and Martin theories [13, 14] of the extended Debye model. However, the dynamic behaviour of the LC dipole can be deciphered from an effective analysis through the proposed study of temperature dependence of low-frequency dispersion. Cole's modified [15] theory of static dielectric permittivity for irreversible processes explains the low frequency dielectric LC relaxations. But, the Cole–Cole theory [9] of complex permittivity is found more relevant to the observed off-centred LC dispersions through the equation given by

$$\varepsilon^*(\omega) = \varepsilon_\infty - \{\Delta\varepsilon/[1 + (i\omega\tau)^{1-\alpha}]\} \qquad (1)$$

where $\varepsilon^* = (\varepsilon' - i\varepsilon'')$ corresponding to the observed ε' and ε'' (from tan Δ) at an oscillating field frequency $\omega = 2\pi f$; $\Delta\omega = [\omega_0 - \omega_\infty]$, with ω_0 and ω_∞ being the values of static low frequency dielectric permittivity and permittivity at the high frequency end; τ is the mean relaxation time. The distribution parameter α reflects the molecular degrees of freedom helpful in studying the dipolar behaviour and its assymmetric response to applied electric fields.

3. Experimental

The *n*O.*m* compounds were synthesized from the appropriate alkoxybenzaldehydes and alkylanilines as reported earlier [16]. The general molecular formula and the dipoles associated with it are given by



The dielectric cell was made with transparent tin oxide coated glass plate electrodes separated by a steel wire of 100 μm gauge. The resistance offered by the tin oxide plates was found to be 4 kΩ cm^{-1}. Dielectric dispersion measurements were carried out with a HP 4192 LF Impedence Analyser (5 Hz to 13 MHz) used with the HP 1604SC test leads kit. The empty cell capacitance and the lead capacitance were determined with standard organic liquids (AR grade). An Instec mK temperature controller (accurate to 10 mK), monitored through a PC, was used for measurement of temperature variation. The empty cell capacitance was found to vary by $<1\%$ in the temperature range 25–150°C. The frequency response of the empty cell, through the permittivity ε' and loss factor tan Δ, was found to be constant (varied by less than 1%) from 40 kHz to 7 MHz. The effective area of the LC material exposed to the applied electric field was found to be 1 cm^2. The cell was dried in an oven and then filled with LC sample at its isotropic liquid temperature by capillary action. The proposed parallel field studies were carried out in the homeotropic geometry of the sample in the cells. Homeotropic alignment of the sample was obtained by exposing the sample to successive cooling runs (at a rate of 0·1 K min^{-1}) from its isotropic liquid state in a magnetic field of 5 kG strength.

4. Results and discussion

4.1. *Temperature variation of permittivity and loss*

The observed variation of dielectric constant and loss as a function of temperature is presented (for the 8O.6 compound as representative) in figure 1. The temperature variation of the low frequency dielectric constant is found to be accompanied by an anomaly at the LC

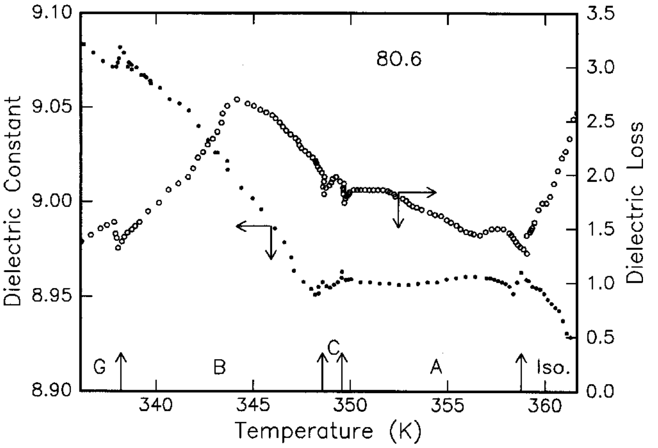


Figure 1. Temperature variation of dielectric constant (permittivity ε') and dielectric loss; phase transition temperatures are marked for the compound 8O.6.

phase transition. The observed dielectric anomaly is due to the molecular dipolar reorganization in the formation of a structurally different phase. The phase transition temperatures identified through the dielectric anomaly (table 1) are found to be in agreement with those determined by other methods. It may be recalled that inter-smectic transitions involving structural changes from an orthogonal arrangement of molecules to a tilted arrangement (viz. of smectic A to smectic C type) are found to be accompanied by a very small (or un-noticeable) enthalpy at the transition, with a faint DSC peak. As such, the detection and identification of smectic A–C transition is rather difficult by usual calorimetric methods. However, the dielectric method is found to be capable of detecting such transitions. Also owing to the fact that it involves the measurement of a dielectric response that reflects even the slightest change of dipolar modulation, this could be a preferred method. The inter-smectic transitions identified by their dielectric anomaly are shown by inset arrows from the temperature axis in figure 1. Further, the observed anomalous increase of ε' at the isotropic to smectic A transition and at the subsequent inter-smectic transitions, with decreasing temperature, has been attributed [17] to the change of the relative strength of dipolar correlation involving long and short range interactions. It is observed that the loss factor is found to decrease with a decrease in temperature at the phase transitions, reflecting the loss of molecular rotational degrees of freedom accompanying the structural change. The observed trends of ε and the loss factor are found to be rather inconsistent at the growth of smectic G phase. This inconsistency may be due to the highly viscous and sticky nature of the G phase or loss of alignment of the sample.

The observed dielectric loss (in arbitrary units) as a function of applied field frequency (1 kHz to 10 MHz) in smectic A, C, F, B (soft crystal), G (soft crystal) phases at specified temperatures is given in figure 2 (for the compound 8O.6 as representative).

Table 1. Phase transition temperatures for LC compounds determined by the dielectric method along with the relevant data from [TM] and {DSC} methods.

	Transition temperatures						
Compound	I-A	A-C	C-B	C-F	B-G	F-G	G-solid
8O.6	359·06	349·67	348·63		338·06		
	[359·15]	[348·75]	[347·95]		[333·95]		[317·65]
	{358·55}	{346·95}			{336·55}		
8O.7	360·85	347·35	347·05				
	[359·95]	[347·55]	[347·35]		[331·15]		
	{357·95}		{347·35}		{329·55}		{302·25}
9O.6	359·63	353·44		350·03		347·63	
	[360·15]	[353 65]		[350·65]		[348·15]	[322·15]
	{357·95}	{351·55}		{348·45}			{323·15}
10O.8	365·99	361·11		359·30		358·10	
	[365·85]	[360·75]		[358·95]		[358·35]	[318·05]
	{362·25}			{355·45}			{315·45}
10O.9	364·75	360·55	358·84		356·56		
	[364·15]	[360·15]	[358·15]		[356·15]		[313·15]
	{364·15}		{357·94}		{356·72}		{312·09}
10O.10	362·15	359·65		358·54		357·76	
	[362·15]	[359·25]		[358·15]		[357·95]	[328·15]
	{361·95}			{357·25}			{326·15}

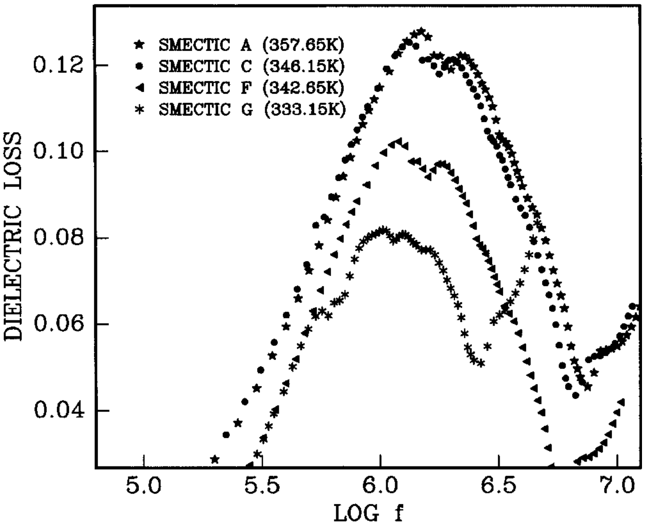


Figure 2. Frequency dependence of dielectric loss in the compound 8O.6 in the smectic phases.

The dielectric loss studied in these LC compounds is found to exhibit two peaks between 500 kHz and 5 MHz which are both found to shift to a lower frequency as one proceeds to low temperature smectic (C, F, B, G) phases from the high temperature smectic A phase. The observed loss peaks and the corresponding Arrhenius-type shift suggest the LC related relaxations are characteristic of the underlying dipolar reorientation mechanism about the molecular long axis. However, it is also noticed (figure 2) that the dielectric loss is accompanied by an increase at the low frequency (<40 kHz) and high frequency (>7 MHz) tail ends of the spectrum; this suggests a possible relaxation process which cannot be completely observed due to the instrumental limitations. However, an overview of the observed loss spectrum (figure 2) of the LC against the background picture of empty-cell loss (found to be almost constant between 490 kHz and 7 MHz) readily suggests the presence of non-LC-like contributions, perhaps from the presence of trace ionic impurities or the conductivity coating of the cell plates. In the wake of the reported [12] smectic multiple relaxation in *n*O.*m* compounds (using the same type and geometry of cells), the observed tail end portion of the loss spectra has been treated to the following reported fitting procedure [18] for the separation of non-LC contributions.

4.2. *Elimination of non-LC contributions*

The data of tail end (<40 kHz and >7 MHz) loss spectra is fitted to a power law relation given by

$$\varepsilon'' \propto f^{d}. \qquad (2)$$

Dielectric loss and log dielectric loss against log frequency, along with the fitted solid line (<40 kHz) and dashed line (>7 MHz) are presented in figure 3 (as representative for the compound 8O.6 in the smectic A phase at specified temperature). The estimated *d* values for different compounds are presented in table 2. The values of *d* clearly suggest that the observed tail end increase in the loss spectrum is characteristic of non-LC nature. Further, the obtained *d* values in comparison with the earlier [18] reports confirm their origin to be due to the presence of ionic impurities (40 kHz) and conductivity coating (>7 MHz).

4.3. *Dielectric dispersion in smectic LC phases*

The two smectic loss peaks accompanied by the Arrhenius shift are found [12] to be characteristic of different and distinct orientational relaxation mechanism involved in the dipolar reorientation processes. The higher frequency and lower frequency loss peaks with their corresponding relaxation frequencies are designated as type I and type II, respectively; results are presented in table 3. Since the two peaks are rather close, the

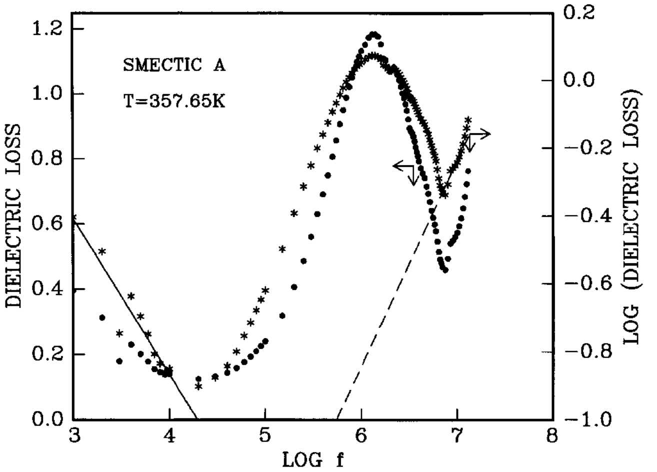


Figure 3. Log frequency versus dielectric loss (●) and versus log dielectric loss (✳); the fitted solid (or dashed) line gives the determination of non LC contribution in the smectic-A phase of compound 8O.6.

Table 2. The values of *d* (contributions from ionic impurities and conductive coating as negative and positive slope values) in equation (2) of text for the determination of the range of LC relaxations.

	d value	
Compound	Low frequency	High frequency
8O.6	0·457	0·607
8O.7	0·834	0·990
9O.6	0·922	0·989
10O.8	0·880	0·480
10O.9	—	0·910
10O.100	0·980	0·960

Table 3. Observed smectic relaxation frequencies at the noted absolute temperatures, [ ], in various liquid crystal phases of *n*O.*m* compounds.

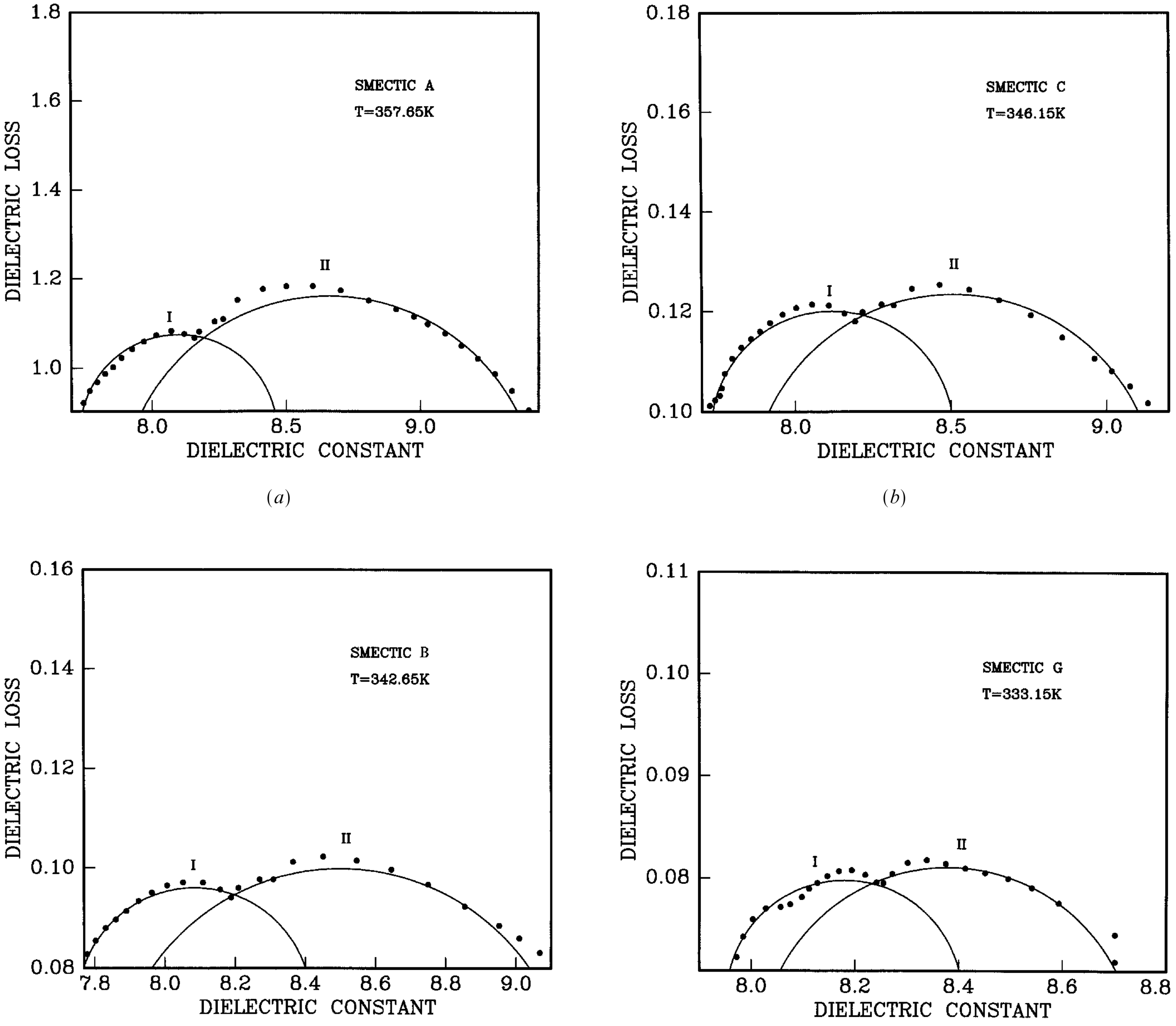
Compound	Relaxation frequency f_R/MHz							
	Smectic A		Smectic C		Smectic B		Smectic F or G#	
	Type I	Type II	Type I	Type II	Type I	Type II	Type I	Type II
8O.6	3·55	2·95	3·52	2·85	2·30	1·5	2·280	1·45
	[357·65]		[349·15]		[342·65]		[333·15#]	
8O.7	1·40	0·85	1·35	0·825	—		—	
	[358·15]		[347·15]					
9O.6	1·16	0·90	1·14	0·86	—		—	
	[359·15]		[352·15]					
10O.8	4·20	3·0	4·0	2·90	—		3·90	2·85
	[363·15]		[360·15]				[357·15]	
10O.9	1·35	0·88	1·30	0·85	—		—	
	[363·15]		[359·15]					
10O.10	1·16	0·60	1·15	0·58	—		—	
	[361·15]		[358·65]					

Cole–Davidson [19] method is applied to resolve the two relaxation mechanisms, i.e. by fitting the high frequency data of type II relaxation separately to the Cole–Cole relation. This procedure is characteristic in excluding the loss data pertaining to the region of interference between them. The Cole–Davidson resolved Cole–Cole plots corresponding to type I and type II relaxations are presented in figures 4 (*a–d*), in their smectic A, C, B and G phases respectively (for the compound 8O.6 as representative). In the wake of LC dielectric experimental observations regarding low temperature metastable solid modifications [20], the occurrence of monotropic transitions [21], the effective role of a transverse dipole in the complex and differentiated reorientation mechanism [22], and the smectic multiple relaxation phenomena [12], the observed Cole–Cole plots (with off-centred arcs and α not equal to 0) suggest a distinct response associated with the dipoles situated at different parts of the liquid crystal molecule. The differing dipolar response of the dipole is explained as one comprising a fast type I mechanism associated with the rigid core LC matrix, and the other a relatively slow type II mechanism associated with a flexible end chain. The observed multiple relaxation phenomenon, with its distinctive time regimes, is suggestive of the inadequacy of the point polarizability concept of bulk or macro-like LC molecules about which the electronic distribution is assymmetric, resulting in a complicated dipolar behaviour. However, the observed comparatively instantaneous reorientation of the rigid core dipole of the LC molecule suggests a more rigid fixation of the molecular body at its central rigid core than at its flexible end chains.

4.4. *Effect of a longer flexible end chain on smectic relaxation frequency*

The data of relaxation frequencies presented in table 3 provide an opportunity to study the effect of increase of alkoxy chain length and alkyl chain length on smectic relaxations. It can be seen that the comparison of f_R can be made in smectic A and C phases only, as they are the common occurring phases in these compounds. From the bare data of both the type I and type II relaxations (from table 3) of smectic A and C phases, it is seen that the increase of alkoxy or alkyl flexible chain results in decreasing relaxation frequency. It is interesting to note that the even numbered *n*O.*m* members (8O.6 and 10O.8) combined with either $n=8$ or $m=8$ are found to bear relaxation frequencies almost three times stronger than the other compounds. This striking difference for the time regime of dipolar dynamics is due to the odd–even effect as detailed by Marcelja [10]. It should be noted that the data in table 3 for the smectic A and C relaxation frequencies correspond to different temperatures (357·65 K in 8O.6 and 359·15 K in 9O.6 in smectic A; 349·15 K in 8O.6 and 352·15 K in 9O.6 in smectic C, etc.) and hence cannot be compared without reducing the data (within the reported [12] Arrhenius dependence).

The usual method for designing a normalized temperature to be used as the relevant variable involves taking its two extremes, 0 being its melting point and 1 its clearing temperature. For a smectic A phase that is formed from isotropic liquid (at T_{IA}) and exists up to the smectic A to smectic C transition (at T_{AC}), any physical property of interest (in the smectic A phase) may be studied as a function of a universal scale given



(*a*) (*b*)

(*c*) (*d*)

Figure 4. Cole–Cole plots for type I and type II relaxations for compound 8O.6 in the smectic A(*a*), C(*b*), B(*c*) and G(*d*) phases.

by $T^{U} = [T_{IA} - T_{i}]/[T_{IA} - T_{AX}]$, where T_{i} corresponds to any temperature of interest and $T_{AX} = T_{AC}$ in the present case of any compound exhibiting a smectic A to smectic C transition. However, for an observed T_{i} in the smectic C phase (occuring between T_{AC} and T_{CF}), the normalized scale $T^{U} = [T_{AC} - T_{i}]/[T_{AC} - T_{CX}]$, where $T_{CX} = T_{CF}$. It may be noticed that for the compound 10O.8, the T_{IA}=365·99 K and T_{AC}=361·11 K (table 1); the normalized universal temperature is found to be 0·5819, corresponding to the observed smectic A dispersion (table 3).

It has been seen [12] that the Arrhenius temperature dependence of the smectic A (from compound 10O.8) relaxation frequency for type I (through the reported activation energies in [12]) is found to correspond to an increment of $3 \times 10^{-3} \log(f)$ for a decrement of universal normalized temperature T^{U} of 0·1808. It is also noticed that in the case of the smectic C phase of compound 10O.8 the frequency increment of $7 \times 10^{-4} \log(f)$ is relatively small for a decrement of normalized temperature of 0·8842. The computed normalized temperature points corresponding to the observed dispersions (as

Table 4. Normalized temperatures corresponding to the observed type I dispersion and estimated values of relaxation frequency in smectic A and C phases for nO.m compounds.

	Smectic A		Smectic C	
Compound	$^{a}T^{U}$/K	f/MHz	$^{a}T^{U}$/K	f/MHz
8O·6	0·1368	3·50	0·3000	3·52
8O.7	0·1496	1·38	0·6666	1·35
9O·6	0·1527	1·15	0·2813	1·14
10O·8	0·4912	4·20	0·0370	4·00
10O·9	0·3333	1·34	0·7500	1·30
10O·10	0·4137	1·16	0·6666	1·15

[a] For definitions of T^{U} for smectic A and smectic C cases see §4.4.

given in table 3) are provided in table 4. It is noted that the normalized temperature points for type I relaxation in smectic A and C phases are found to differ. Hence, in the style of a linear Arrhenius relation between reduced temperature and log(f_R), and using the observed increment of log(f) for a decrement of T^{U} in the smectic A and C phases of compound 10O.8, the relaxation frequency is estimated at a common normalized temperature point for the sake of comparison, i.e., 0·4912 in smectic A and 0·037 in smectic C phases. The estimated smectic A and C relaxation frequencies (corresponding to the observed dispersions at different temperatures of different compounds), extrapolated following Arrehenius behaviour to a common normalized temperature, are provided in table 4. It is observed that the type I relaxation frequency, corresponding to the rigid core part of the LC molecule in a smectic A or C phase, is found to shift to lower frequency with increasing alkyl (8O.6 to 8O.7 and 10O.8, 10O.9 to 10O.10) or alkoxy (8O.6 to 9O.6) chain length. However, the shift is found to be rather steep when the chain length increase involves the alkoxy chain. It may be seen that the analysis and estimation of type II relaxations are not carried out, since the reported Arrehenius dependence through their activation energies [12] corresponds to type I only. Further, it is also noted that the trend of migration of smectic orientational relaxations suggests that the dipole associated with the central rigid core experiences a differing LC environment due to the varied chemical environment induced by the increasing end chain. The present case of an essentially rigid core dipolar reorientation with varied flexible part is analogous to the problem of studying the effect of induced polarizability [23] on solute particles (rigid core) by varying the solvent concentration in a solution.

The authors are grateful for financial assistance provided by AICTE and DST, New Delhi.

References

[1] Litster, J. D., Birgeneau, R. J., and Pershan, P., 1982, in *Physics Today*, May; Brock, J. D., Birgeneau, R. J. Litster, J. D., and Aharany, A. H., 1989, in *Physics Today*, July, 52.

[2] Meier, G., Sackmann, K., and Gragmaier, J. G., 1975, in *Applications of Liquid Crystals* (Springer), p. 150.

[3] Gray, G. W., 1978, in *Advances in Liquid Crystal Materials for Applications*, BDH Monograph.

[4] De Jeu, W. H., 1978, in *Dielectric Permittivity of Liquid Crystals, Solid State Physics Suppl*., **14,** 109.

[5] Clark, N. A., and Lagerwall, S. T., 1990, in *Ferroelectric Liquid Crystals, Principles, Properties and Applications* (Gordon & Breach), p. 49.

[6] Gray, G. W., 1979, in *Molecular Physics of Liquid Crystals*, edited by G. R. Luckhurst and G. W. Gray (Academic Press), p. 1.

[7] Kresse, H., 1983, in *Advances in Liquid Crystals*, edited by G. H. Brown (New York: Academic Press), p. 109.

[8] Bond, M. F., Price, A. H., Clark, N. A., and McDonnel, D. G., 1984, in *Liquid Crystals and Ordered Fluids* (Plenum), p. 799.

[9] Hill, N. E., Vaughan, W. E., Price, A. H., and Davies, M., 1969, in *Dielectric Properties and Molecular Behaviour* (New York: Von Nostrand Reinhold), pp. 49, 53 and 54.

[10] Marcelja, S., 1974, *J. chem. Phys*., **60,** 3599.

[11] Kresse, H. S. E., Wedler, W., Demus, D., and Kremer, F., 1990, *Ber. Bunsenges. phys. Chem*., **94,** 1478.

[12] Rani, G. P., Potukuchi, D. M., Rao, N. V. S., and Pisipati, V. G. K. M., 1994, *Solid State Commun*., **92,** 349 and references therein.

[13] Maier, W., and Meier, G., 1961, *Z. Naturforsch*., **16a,** 262, 470; Maier, W., and Saupe, A., 1959, *Z. Naturforsch*., **14a,** 882; Maier, W., and Saupe, A., 1960, **15a,** 287; Maier, W., and Saupe, A., 1966, *Mol. Cryst. liq. Cryst*., **1,** 515.

[14] Martin, A. J., Meier, G., and Saupe, A., 1971, *Symp. Faraday Soc*., **5,** 119.

[15] Cole, K. S., and Cole, R. H., 1941, *J. chem. Phys*., **9,** 341; Cole, R. H., 1965, *J. chem. Phys*., **43,** 637.

[16] Pisipati, V. G. K. M., Rao, N. V. S., Sastri, B. C., Rao, P. B., Rani, G. P., and Alapati, P. R., 1991, *Liq. Cryst*., **9,** 565; Pisipati, V. G. K. M., Rao, N. V. S., Rani, G. P., and Rao, P. B., 1991, *Mol. Cryst. liq. Cryst*., **210,** 165.

[17] Doucet, J., 1979, *J. de Phys. Lett*., **40,** L-185.

[18] Gouda, F., Skarp, K., and Lagerwall, S. T., 1991, *Ferroelectrics*, **113,** 165; Gouda, F., Skarp, K., Lagerwall, S. T., Escher, C., and Kresse, H., 1991, *J. de Phys*., **11,** 167.

[19] Cole, R. H., and Davidson, D. W., 1952, *J. chem. Phys*., **20,** 1389; Kresse, H., and Moscicki, J. K., 1980, *Advances in Liquid Crystal Research and Applications* (Oxford: Pergamon Press), p. 287.

[20] Agarwal, V. K., Arora, V. P., and Mansingh, A., 1978, *Mol. Cryst. liq. Cryst*., **45,** 117.

[21] Rujmetsev, E. I., and Kovshik, A. P., 1995, *Liq. Cryst*., **18,** 819.

[22] Kresse, H., Tshierske, S., Hohmuth, A., Stutzer, C., and Weissflog, W., 1996, *Liq. Cryst*., **20,** 715; Bauman, D., Kedziora, P., Legrande, C., and Jadzyh, J., 1996, *Liq. Cryst*., **21,** 389.

[23] Glasstone, S., 1991, in *Text Book of Physical Chemistry* (MacMillan), p. 550.