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Polarization–tilt coupling of a ferroelectric liquid crystal with varying molecular configuration

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Abstract

At large tilt angles the coupling between the spontaneous polarization and the tilt of ferroelectric liquid crystals exhibits nonlinear behaviour. This is theoretically described by the *generalized* Landau model, which introduces a bilinear and a biquadratic coupling term, the latter describing transversal quadrupolar order. We have investigated a ferroelectric liquid crystal with two chiral centres, systematically varying the chiral centres, to elucidate both the influence of molecular *configuration* and *constitution* on the coupling between polarization and tilt. It is shown experimentally that the bilinear coupling term depends strongly on the molecular configuration (chirality) of the mesogen, while the molecular constitution determines the achiral biquadratic coupling.

1. Introduction

Due to their applicational potential for fast switching display and other electro-optic devices, but especially also for their intriguing fundamental physical properties as the only known polar liquids, ferroelectric liquid crystals [1, 2] have attracted much research interest over the last 25 years. It was first established by Meyer *et al* [3] that for symmetry reasons chiral tilted smectic phases can exhibit a spontaneous polarization P_S and thus pyroelectric properties. If this polarization can be reversed between two stable states under application of electric fields, we speak of ferroelectricity and ferroelectric liquid crystals (FLCs). This behaviour was first realized by Clark and Lagerwall [4] when introducing the surface stabilized geometry of ferroelectric liquid crystals (SSFLCs) and unwinding the intrinsic zero-voltage helical superstructure of the SmC^* phase by surface interactions through closely spaced substrates (cell gap smaller than the helical pitch).

The tilt angle θ of the SmC^* phase, i.e. the angle between the direction of the average long molecular axis called the director n and the smectic layer normal k , is the primary order parameter in the description of the phase transition into the ferroelectric phase (figure 1). The spontaneous polarization P_S represents a secondary order parameter, in close analogy to

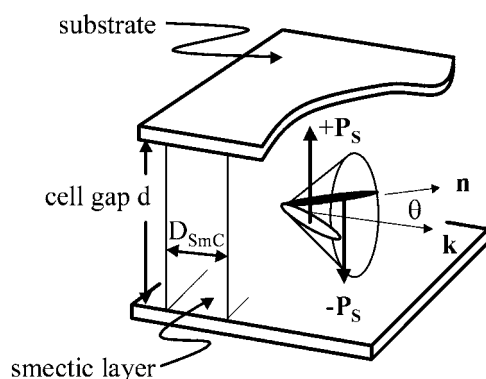


Figure 1. Schematic illustration of the surface stabilized ferroelectric SmC* liquid crystal geometry with tilt angle $\theta(T)$ and spontaneous polarization $P_S(T)$, the primary and secondary order parameters for the transition into the ferroelectric phase.

ferromagnetic systems, where the magnetization M is employed as order parameter to describe the transition into the ferromagnetic phase. The sole reason why in ferroelectric liquid crystals the tilt angle θ is the preferred order parameter as compared to the spontaneous polarization P_S lies in the fact that only chiral materials may exhibit a spontaneous polarization, while also achiral SmC materials exhibit a tilt angle θ . This disregards the special case of the recently discovered ‘banana phases’ [5] observed for bent-core mesogens, which have been shown to exhibit ferroelectric/antiferroelectric behaviour despite the achiral nature of their comprising mesogens [6].

At the transition into the SmC liquid crystalline phase the classic Landau theory describes the free enthalpy density g as an expansion of the (achiral) order parameter θ :

$$g = g_0 + \frac{1}{2}a\theta^2 + \frac{1}{4}b\theta^4 + \frac{1}{6}c\theta^6 + \dots \quad (1)$$

where g_0 is the free enthalpy density of the high temperature phase. The Landau coefficients are generally regarded as temperature independent, with the exception of the first coefficient, which varies linearly as $a = \alpha(T - T_C)$ and reverses its sign at the transition into the ferroelectric phase at T_C . It is $b > 0$ for a second order, while it is $b < 0$ for a first order phase transition, while $c > 0$ in all cases [7, 8]. Considering chiral materials, the occurrence of a local polarization and the formation of a helical superstructure with wavevector q_0 has to be taken into account. In this study the latter can be neglected, because investigations were carried out in the surface stabilized geometry [4] where the helix is suppressed by the boundary conditions, i.e. $q_0 = 0$. The coupling between polarization and tilt is generally described by a bilinear term $-CP\theta$, with C being the piezoelectric coupling coefficient and P the total polarization. The C -coefficient is *chiral* in nature. Away from the direct vicinity of the transition the total polarization P is approximately equal to the spontaneous polarization P_S , because the electroclinic effect [9] vanishes quickly, thus $P = P_S$. The linear polarization–tilt coupling is only observed in the regime of small tilt angles. The experimentally observed nonlinear behaviour at larger tilts [10] is accounted for by the ‘generalized Landau theory’ [11, 12], which introduces a biquadratic coupling term $-\Omega P^2\theta^2/2$ with Ω the quadrupolar coupling constant, which is *achiral* in nature. The free enthalpy expansion of a surface stabilized ferroelectric liquid crystal is thus given by

$$g = g_0 + a\theta^2 + b\theta^4 + c\theta^6 + \frac{P^2}{2\chi} - C\theta P - \frac{\Omega P^2\theta^2}{2} \quad (2)$$

where a dipolar ordering term $P^2/2\chi$ (with χ the dielectric susceptibility at large frequencies) and the bilinear and the biquadratic coupling terms are added to equation (1). Using $P = P_S$ and minimizing equation (2) with respect to the polarization we obtain the following relation between the spontaneous polarization and the tilt:

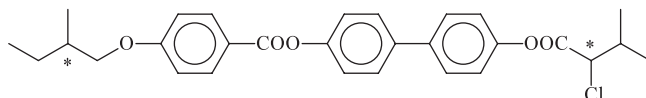
$$P_S \approx \frac{\chi C \theta}{1 - \chi \Omega \theta^2}. \quad (3)$$

Employing a nonlinear least squares fit to experimental $P_S(\theta(T))$ data the linear, chiral (χC) and the nonlinear, achiral ($\chi \Omega$) contributions towards polarization–tilt coupling can be determined.

In this study we investigate a specially designed molecule with two chiral centres which can independently be varied in their *configuration* and thus allow the determination of the polarization–tilt coupling contributions at varying chirality, while the molecular *constitution* remains unchanged. To our knowledge this is the first experimental investigation of the chiral/achiral nature of the bilinear/biquadratic coupling contributions, respectively.

2. Experimental details

The compound investigated in this study (abbreviated as M96) is a benzoic acid biphenyl ester with the following structural formula:



The material contains two chiral centres, one on each side of the mesogenic core, which can be chemically varied independently of each other. The following five configurations were studied: (S, S), (S, R), (S, rac), (rac, S) and (rac, R), where ‘rac’ indicates the racemic configuration of an individual chiral centre. Note that these compounds are *diastereomers*, thus exhibit (slightly) different clearing points and chirality related properties. Only the (rac, S) and (rac, R) configured materials are *enantiomers* with equivalent phase transition temperatures and equal, but opposite, chiral properties. The synthesis, detailed characterization and some physical properties have been reported elsewhere [13, 14].

Samples were investigated after capillary filling of commercially available sandwich cells from EHC, Japan, with a cell gap of $d = 4 \mu\text{m}$. Polarizing microscopy (Olympus BH-2) confirmed the suppression of the helical SmC^* superstructure. Relative temperatures for polarization measurements were controlled to an accuracy of $\pm 0.1 \text{ K}$ by a Mettler FP-52 hot stage. Determination of the temperature dependence of the spontaneous polarization was carried out by the well known triangular wave method [15] at an electric field amplitude of $E = 5 \text{ MV m}^{-1}$ and frequency $f = 200 \text{ Hz}$. Tilt angles were determined by x-ray investigations of the SmC^* layer spacing D_{SmC} (Kratky camera Anton Paar KG, Cu $K\alpha$ radiation and a one-dimensional position sensitive counter, Firma M Braun), taking the length $L = 26.7 \text{ \AA}$ of the fully extended molecular configuration as the layer spacing of the non-tilted phase. The tilt angle can then be calculated from $\theta = \arcsin(D_{\text{SmC}}/L)$. The temperature resolution of the x-ray investigations is estimated to $\pm 0.5 \text{ K}$. The investigated materials exhibit a first order transition into the ferroelectric liquid crystal SmC^* phase. This makes it difficult to experimentally obtain reliable tilt angle measurements in the very close vicinity ($T_C - T < 1 \text{ K}$) of the phase transition by electro-optic techniques, due to smectic layer instabilities and the formation of horizontal chevrons. Therefore, tilt angles were determined by x-ray investigation, despite the somewhat poorer temperature resolution. Nevertheless, tilt angle data were collected up to reduced temperatures of $T_C - T = 1 \text{ K}$. This procedure is

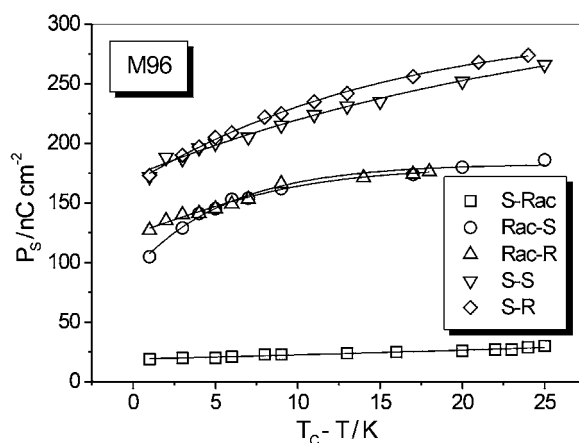


Figure 2. Magnitude of the spontaneous polarization P_S as a function of reduced temperature $T_C - T$ for all five different configurations of M96: \square (S, rac), \circ (rac, S), \triangle (rac, R), ∇ (S, S) and \diamond (S, R). Solid lines are a guide to the eye. Note that the (rac, S) and (rac, R) configured compounds are *enantiomers*, exhibiting equal transition temperatures and equal chiral properties at opposite sign, while the (S, S) and (S, R) configured compounds are *diastereomers*, which exhibit different transition temperatures and chiral properties.

further justified by the fact that the employed approximation of $P = P_S$ would become less valid in the very close vicinity of the transition, due to the electroclinic effect.

3. Experimental results and discussion

Five different chiral configurations of the molecule M96 were investigated: (i) (S, rac) with only the left chiral centre being active, the two enantiomers (ii) (rac, S) and (iii) (rac, R) with only the right chiral centre being active at mutually opposite configuration and finally the diastereomers (iv) (S, S) and (v) (S, R) with both chiral centres being active. The synthesis of materials with the left chiral centre in R-configuration, i.e. compounds (R, rac), (R, S) and (R, R), is unfortunately impossible, because the respective chiral precursor alcohol is not available, nor does it seem to have ever been synthesized successfully.

Figure 2 depicts the spontaneous polarization P_S as a function of reduced temperature $T_C - T$, where T_C is the transition temperature to the ferroelectric SmC* phase. As expected, the enantiomers (rac, S) (circles) and (rac, R) (up triangles) exhibit equal magnitudes of the polarization values, although their signs are indeed opposite, with that of (rac, S) being positive and that of (rac, R) negative, determined according to the convention introduced in [16]. Compared to the relatively large chiral contribution of the right chiral centre with the C–Cl group, that of the left centre (S, rac) (squares) is quite small, due to the much smaller lateral dipole moment of the C–CH₃ group. The polarization of the left chiral centre in S-configuration is negative. The two diastereomers (S, S) (down triangles) and (S, R) (diamonds) exhibit an even larger magnitude of the spontaneous polarization, although slightly different in value. They show values which are roughly equivalent to the sum of the contributions of the two individual chiral centres, when taking into account their respective signs. The polarization of (S, S)-M96 is positive and that of (S, R)-M96 negative. The relative contributions of the two chiral centres to the overall molecular chirality are additionally evidenced by the pitch behaviour (magnitude and sign) of the cholesteric phase as pointed out in [13].

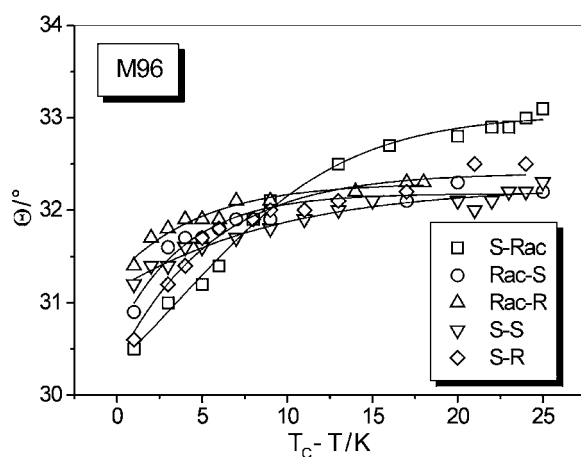


Figure 3. Tilt angle θ as a function of reduced temperature $T_C - T$ for all five different configurations of M96: \square (S, rac), \circ (rac, S), \triangle (rac, R), ∇ (S, S) and \diamond (S, R). Solid lines are a guide to the eye. The tilt angle is the primary order parameter of the transition into the ferroelectric phase and it is non-chiral in nature, thus practically exhibiting the same temperature dependence for all compounds under investigation.

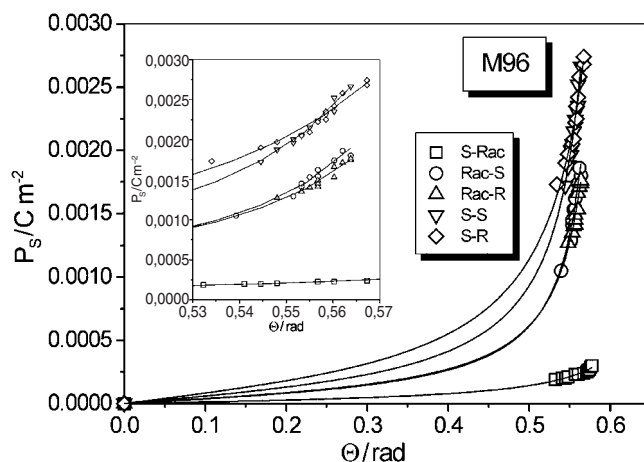


Figure 4. Spontaneous polarization P_S as a function of tilt angle θ for all five different configurations of M96: \square (S, rac), \circ (rac, S), \triangle (rac, R), ∇ (S, S) and \diamond (S, R). Solid lines represent a least squares fit to equation (3). Due to the first order transition to the ferroelectric SmC^* phase only the behaviour at large tilt angles and polarization is exhibited, exemplifying the nonlinear relationship between the primary and the secondary order parameter.

The tilt angle dependence on reduced temperature $\theta(T_C - T)$ is depicted in figure 3. Being an achiral parameter, the tilt angle is not expected to be very dependent on the configurations of the chiral centres of the respective molecules under investigation. The experimental data of figure 3 confirm this expectation. Due to the first order nature of the transition into the ferroelectric SmC^* phase of M96, the tilt angle as well as the spontaneous polarization exhibit a discontinuous behaviour.

Figure 4 shows the spontaneous polarization P_S as a function of tilt angle θ for all five differently configured molecules of M96 over a temperature range of approximately 25 K

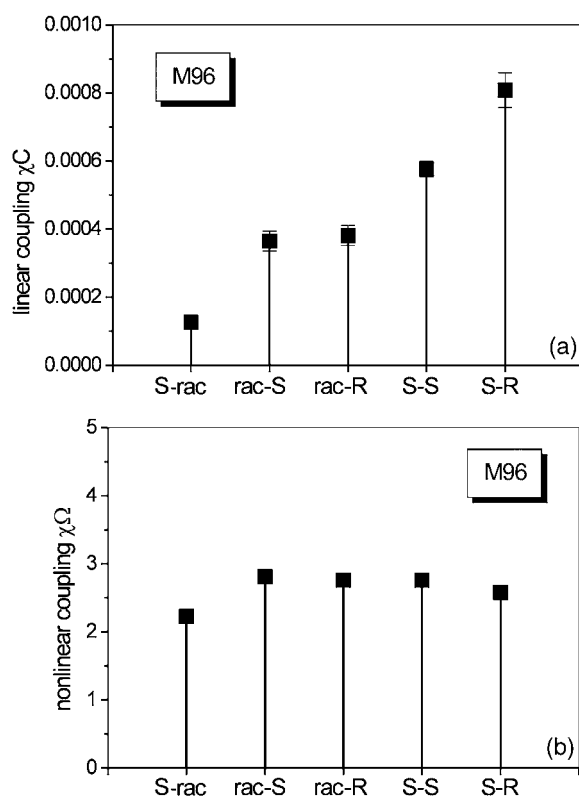


Figure 5. (a) Linear piezoelectric χC and (b) nonlinear quadrupolar $\chi\Omega$ contributions towards the polarization–tilt coupling for the different configurations of M96 investigated. The linear coupling (a) shows a clear dependence on chirality of the constituent molecules, while the quadrupolar coupling (b) is independent of the configuration of the respective mesogens.

into the ferroelectric SmC^* phase. The relations are clearly nonlinear, reflecting the expected deviations for large tilt angles. The two enantiomers (rac, S) and (rac, R) exhibit equivalent polarization–tilt coupling, while the diastereomers (S, S) and (S, R) show slightly differing behaviour. The solid lines in figure 4 represent least squares fits of the experimental data to equation (3), allowing the estimation of the two fit parameters χC and $\chi\Omega$. From the theoretical considerations of the generalized Landau model the former parameter is expected to be chiral in nature, while the latter should not depend on molecular configuration. Table 1 summarizes the respective results obtained from the experimental investigations of all molecular configurations under discussion.

Figures 5(a) and (b) schematically illustrate the linear, piezoelectric and the nonlinear, quadrupolar polarization–tilt coupling contributions, χC and $\chi\Omega$, respectively, for varying molecular configurations of the M96 mesogen. (Values are given in arbitrary units, because the value of χ is not known precisely; nevertheless, this does not affect the general discussion of the behaviour reported.) Referring to the discussion above, the linear polarization–tilt coupling contribution χC clearly unveils its *chiral* nature. It varies considerably for the five different M96 configurations investigated. The linear coupling coefficient is small for the left chiral centre, (S, rac), it is practically equal for the two enantiomers (rac, S) and (rac, R), and it is enhanced for the diastereomeric mesogens (S, S) and (S, R) with both chiral centres being

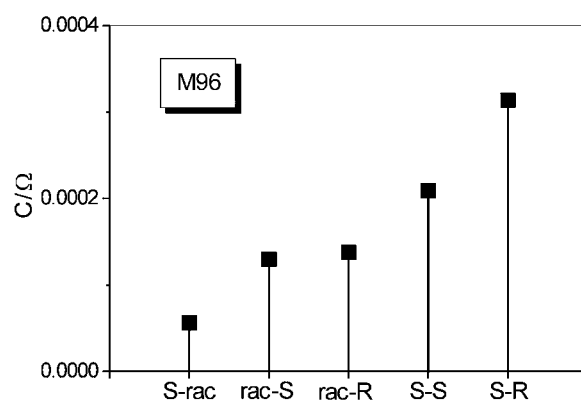


Figure 6. Ratio between the linear and the nonlinear polarization–tilt coupling coefficients, C/Ω , for all different molecular configurations of the investigated compound M96.

Table 1. Linear and nonlinear polarization–tilt coupling contributions for the different molecular configurations of the compound M96.

Molecular configuration	Linear piezoelectric coupling χC (au)	Nonlinear quadrupolar coupling $\chi \Omega$ (au)
(S–rac)	12.6 ± 0.8	2.23 ± 0.06
(rac–S)	36.5 ± 2.9	2.81 ± 0.03
(rac–R)	38.1 ± 2.9	2.76 ± 0.03
(S–S)	57.7 ± 2.3	2.76 ± 0.02
(S–R)	80.9 ± 5.1	2.58 ± 0.04

active (figure 5(a)). The chiral piezoelectric coupling coefficient thus clearly depends on the *configuration* of the mesogens. At the same time the nonlinear, quadrupolar polarization–tilt coupling contribution $\chi \Omega$, which is *achiral* in nature, does not show any appreciable change as the configurations of the chiral centres are varied (figure 5(b)). It is only dependent on the *constitution* and not the configuration of the mesogens. Figure 6 shows the ratio between the linear and nonlinear contributions to the polarization–tilt coupling, i.e. the ratio between the chiral piezoelectric and the achiral quadrupolar coupling constants, C/Ω , for all investigated configurations of M96. From figures 5 and 6 it is evident that polarization–tilt coupling is to first order determined by the molecular configuration and to second order by molecular constitution. The bilinear coupling coefficient C is clearly *chiral* in nature, depending on *molecular configuration*, while the biquadratic coupling coefficient Ω is *achiral* in nature, depending on *molecular constitution*. The former describes linear behaviour, while the latter is responsible for non-linear deviations.

4. Conclusion

We have investigated the polarization–tilt coupling of a mesogen with two chiral centres, which can be chemically varied independently to produce five different molecular configurations of a molecule without varying its molecular constitution. Temperature dependent polarization and tilt angle investigations in the ferroelectric liquid crystal SmC^* phases of respective enantiomers and diastereomers were carried out. They provide the basis for the first experimental evidence of the chiral nature of the bilinear, $-CP\theta$, and the achiral nature of the biquadratic, $-\Omega P^2\theta^2/2$,

coupling terms of the generalized Landau model of ferroelectric liquid crystals. Linear polarization–tilt coupling is due to molecular configuration, while nonlinear behaviour is governed by molecular constitution.

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