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The coupling between polarization and tilt in homologous series of ferroelectric liquid crystals

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Abstract

At temperatures well below the vicinity of the transition to the ferroelectric phase the coupling between the spontaneous polarization of the SmC* phase with the director tilt angle exhibits nonlinear behaviour. In a generalized Landau model of ferroelectric liquid crystals this is theoretically described by two terms in the free enthalpy density expansion: (i) the chiral bilinear or piezoelectric coupling term and (ii) the achiral biquadratic coupling term, which describes the transversal quadrupolar ordering. We have investigated two homologous series of ferroelectric liquid crystals of varying phase sequence with respect to piezoelectric and quadrupolar coupling. It is shown that the linear coupling increases with increasing molecular length, while nonlinear contributions decrease. Effects of varying phase sequences N*–TGBA*–SmA*–SmC* versus N*–SmC* are discussed.

1. Introduction

Ferroelectric liquid crystals (FLCs) [1, 2] have been the subject of intense investigation over the last two decades, not only with respect to their intriguing properties for fundamental condensed matter research, being the only known intrinsic polar fluid materials, but also for application in fast switching flat panel displays or optical light modulators. The most fundamental parameters of an FLC are the tilt angle θ , i.e. the angle between the director and the smectic layer normal, and the spontaneous polarization P_S . The former (θ) is generally considered as being the order parameter to describe the phase transition into the ferroelectric SmC* phase, while the latter (P_S) is a secondary order parameter. This is in close analogy with phase transitions to ferromagnetic systems where the magnetization \mathbf{M} is taken as the primary order parameter. The reason why we chose the tilt angle θ as the primary order parameter for ferroelectric liquid crystals instead of the spontaneous polarization P_S is solely due to the fact that a spontaneous polarization can only occur in *chiral* tilted smectics [3] (disregarding the special case of bent-core or so called ‘banana’ liquid crystals [4]). *Achiral* tilted smectic phases do not exhibit

polar properties, but should nevertheless be described by the same theory of phase transition into the tilted phase, thus the choice of respective primary and secondary order parameters.

For small tilt angles, close to the transition from the paraelectric to the ferroelectric phase, i.e. especially in the vicinity of a second order SmA* to SmC* transition, a linear relation between tilt and polarization is observed, $\theta \sim P_S$. As we cool further into the ferroelectric SmC* phase, deviations from this linear relationship become apparent. Similarly, for the first order transition from N* to SmC*, nonlinear behaviour is observed, especially for materials with a large ferroelectric SmC* phase region, as for the materials studied in this investigation.

The classic Landau theory describes the free enthalpy density g of the non-chiral SmA–SmC transition as an even power law expansion with respect to the (achiral) order parameter θ , given as

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

where g_0 is the free enthalpy density of the high temperature phase and a, b, c are the Landau coefficients, with $a = \alpha(T - T_C)$ a linearly temperature dependent coefficient which reverses sign at the phase transition temperature T_C , $b > 0$ and $c > 0$ [5, 6] (the expansion is generally cut off after the third term in θ). When chiral compounds are considered, we have to take into account the occurrence of a local spontaneous polarization and the macroscopic formation of a helical superstructure with wavevector q_0 . These are secondary order parameters of the chiral SmC* phase and have to be considered in a mean field description of the SmA*–SmC* transition of chiral materials [7]. As we are here investigating materials in the surface stabilized geometry [8], i.e. with the helical superstructure suppressed by boundary conditions ($q_0 = 0$), the respective Landau expansion is given by

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

adding

- (i) a dipolar ordering term $P^2/2\chi$, with χ being the dielectric susceptibility along the electric field direction and P the total polarization, and
- (ii) a bilinear coupling term in tilt and polarization $-CP\theta$, to account for piezoelectric effects (C is the piezoelectric coefficient).

Away from the vicinity of the transition temperature T_C , the electroclinic effect [9] is very small and we can thus neglect the dielectric contribution towards the total polarization P as compared to the spontaneous polarization P_S ; thus $P = P_S$. The above description predicts a linear dependence of the spontaneous polarization P_S on tilt angle θ . This is generally in contradiction to experimental findings, especially for large tilt angles, i.e. far below the transition into the SmC* phase [10, 11]. In the ‘generalized Landau theory’ [12, 13] these deviations were accounted for by quadrupolar ordering, described by the biquadratic coupling term $-\Omega P^2\theta^2/2$, with Ω the quadrupolar coupling constant. The free enthalpy density is then given by

$$g = g_0 + a\theta^2 + b\theta^4 + c\theta^6 + \frac{P^2}{2\chi} - C\theta P - \frac{\Omega P^2\theta^2}{2}. \quad (3)$$

We here neglect a term $1/4\eta P^4$, ($\eta > 0$), which was originally added for stability reasons, but which has no physical justification and has been shown to be insignificant in the description of experimental data [10]. Minimization of equation (3) with respect to the total polarization P (and here $P \approx P_S$, as data were obtained far below the transition into the SmC* phase), gives

$$P_S \approx \frac{\chi C\theta}{1 - \chi\Omega\theta^2}. \quad (4)$$

Table 1. Phase sequences and transition temperatures of the M-series in °C. Note that there are also various higher ordered phases observed [15], which are not relevant to this study and thus are not listed here.

Compound	Iso.		BP*		N*		SmA*		SmC*
M4	•				207.5	•			120.4
M5	•	197.5	•		197.2	•			128.9
M6	•	190.8	•		189.9	•			138.5
M7	•	183.6	•		182.4	•			142.3
M8	•	184.6	•		183.1	•			146.6
M9	•	179.9	•		178.4	•			153.7
M10	•	176.7	•		174.2	•	158.7	•	157.2

Table 2. Phase sequences and transition temperatures of the D-series in °C. Note that there are also various higher ordered phases observed [17], which are not relevant to this study and thus are not listed here.

Compound	Iso.		N*		TGBA*		SmA*		SmC*
D5	•	134.1	•						106.7
D6	•	135.6	•						114.6
D7	•	133.2	•	121.1	•				120.8
D8	•	134.5	•	129.4	•	129.2	•		125.6

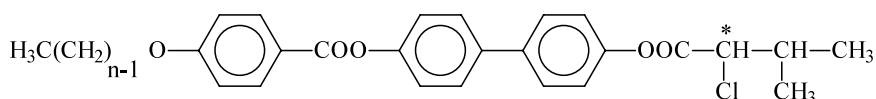
In the present case, flexoelectric contributions are negligible, because the samples were uniformly oriented in bookshelf geometry, i.e. spatial elastic deformations of the director were absent. Plotting $P_S(T)$ versus $\theta(T)$, we can thus determine the linear χC and the nonlinear $\chi\Omega$ contributions towards polarization–tilt coupling by a nonlinear least-squares fit.

In this study, the respective contributions will be determined for compounds of two homologous series of ferroelectric liquid crystals, which exhibit varying phase sequences with increasing molecular length. To our knowledge this is the first study of polarization–tilt coupling for homologous series, actually evaluating the ratio between piezoelectric and quadrupolar effects, especially for series of varying phase sequence.

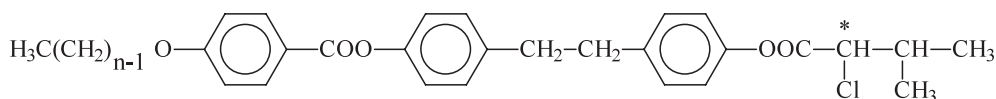
2. Experimental details

The two homologous series investigated have the following general molecular structure.

M-series ($n = 4$ –10, M4–M10):



D-series ($n = 5$ –8, D5–D8):



Their synthesis, characterization and some physical properties have been reported elsewhere (see [14, 15] for the M-series and [16, 17] for the D-series). The relevant parts of the phase sequences of the compounds of both series are summarized in tables 1 and 2, respectively. In relation to the ferroelectric SmC* phase, the D-series exhibits a ‘smooth’ crossover from an N*–SmC* transition (D5, D6) to an SmA*–SmC* transition (D8) for increasing chain length via an N*–TGBA*–SmC* sequence (D7). In contrast, the M-series homologues exhibit mainly

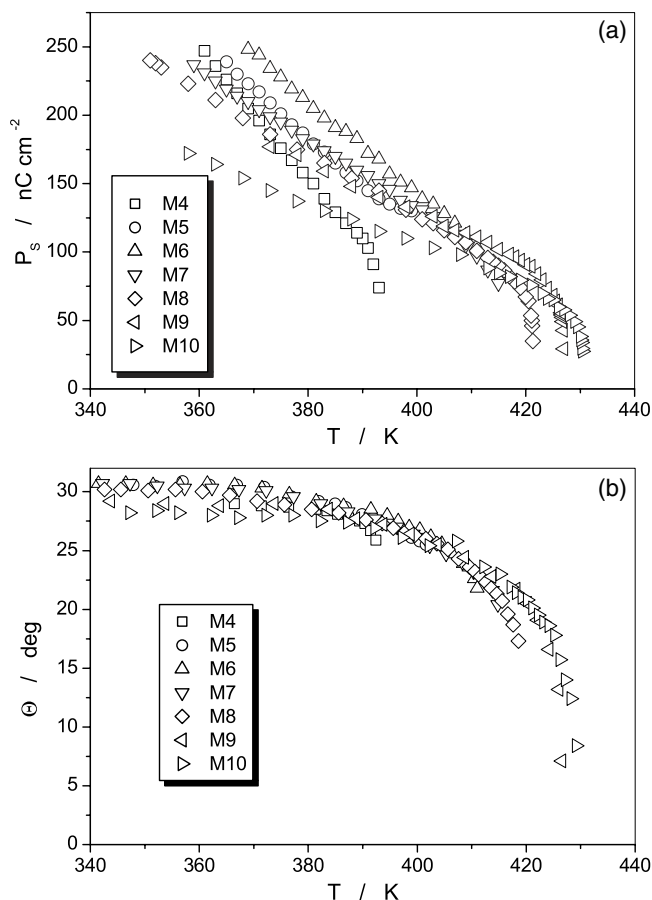


Figure 1. (a) The temperature dependence of the spontaneous polarization P_s and (b) the tilt angle θ of the M-series of homologous compounds, as indicated in the legend of the graphs.

N^* – SmC^* transitions (M4–M9), with a narrow SmA^* phase only being observed for the M10 compound.

Samples were prepared by capillary filling into commercially available sandwich cells (E.H.C., Japan) of cell gap $4 \mu\text{m}$, resulting in good alignment and suppression of the SmC^* helix [8], as confirmed by polarizing microscopy (Olympus BH-2). Temperatures were controlled within $\pm 0.1 \text{ K}$ by a Mettler FP-52 hot stage. Polarization measurements were carried out by the well established triangular wave method [18] at a field amplitude of $E = 3 \text{ V } \mu\text{m}^{-1}$ and frequency $f = 100 \text{ Hz}$ for the M-series and $E = 1\text{--}2 \text{ V } \mu\text{m}^{-1}$ at $f = 200 \text{ Hz}$ for the D-series in order to assure saturated switching. The tilt angles of the SmC^* phase of the M-series were determined from x-ray investigations (Kratky camera Anton Paar KG, $\text{Cu K}\alpha$ radiation and a position sensitive counter, Firma M. Braun), taking the length of the extended molecular configuration as the layer spacing of the non-tilted phase [15]. Tilt angles of the SmC^* phase of the D-series were determined by an electro-optic method introduced by Bahr and Heppke [19], which measures the phase shift between the transmission of the polarization ‘up’ and ‘down’ states as the sample is rotated between crossed polarizers. The phase shift of both curves is equal to 2θ and values were consistent with x-ray investigations of the layer spacing.

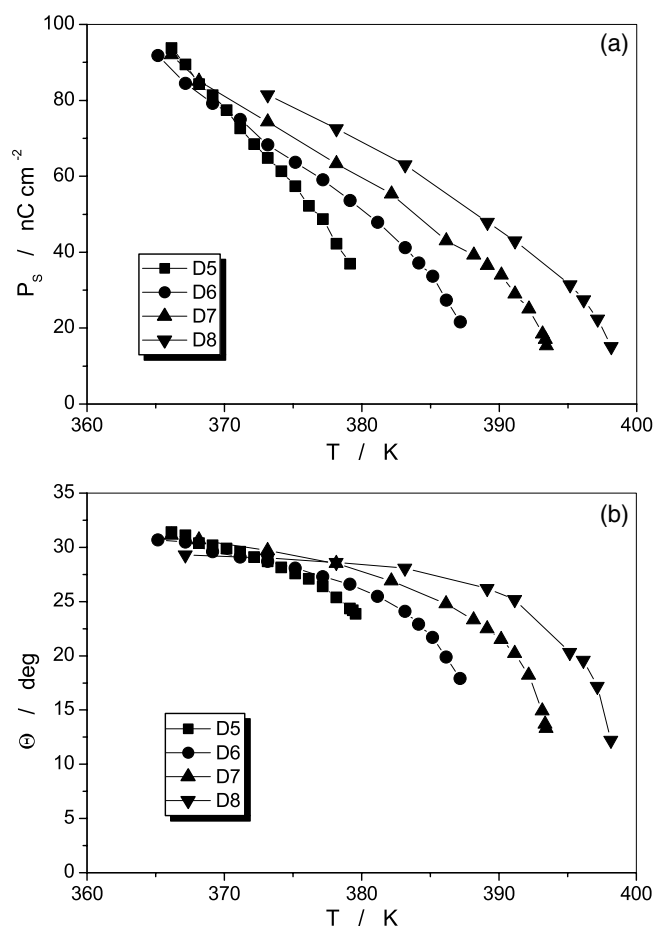


Figure 2. (a) The temperature dependence of the spontaneous polarization P_S and (b) the tilt angle θ of the D-series of homologous compounds, as indicated in the legend of the graphs. (solid lines are a guide to the eye).

3. Experimental results and discussion

Two homologous series were investigated:

- (i) the M-series with an $N^*-\text{SmC}^*$ transition for most homologues (M4–M9) and a sudden change in phase sequence to $\text{SmA}^*-\text{SmC}^*$ for M10, and
- (ii) the D-series, where the change in phase sequence with increasing molecular length is more subtle, changing from $N^*-\text{SmC}^*$ (D5, D6) via $N^*-\text{TGBA}^*-\text{SmC}^*$ (D7) to $N^*-\text{TGBA}^*-\text{SmA}^*-\text{SmC}^*$ (D8).

Figure 1 depicts the temperature dependence of the spontaneous polarization P_S and the tilt angle θ for the M-series, shown in parts (a) and (b), respectively. Different members of this homologous series are indicated by open symbols as described in the legend of the two figures. The data display the typical behaviour observed for SmC^* phases of many calamitic ferroelectric liquid crystals, and we note that the spontaneous polarization still increases at temperatures far below the transition (figure 1(a)), while the tilt angle saturates for low

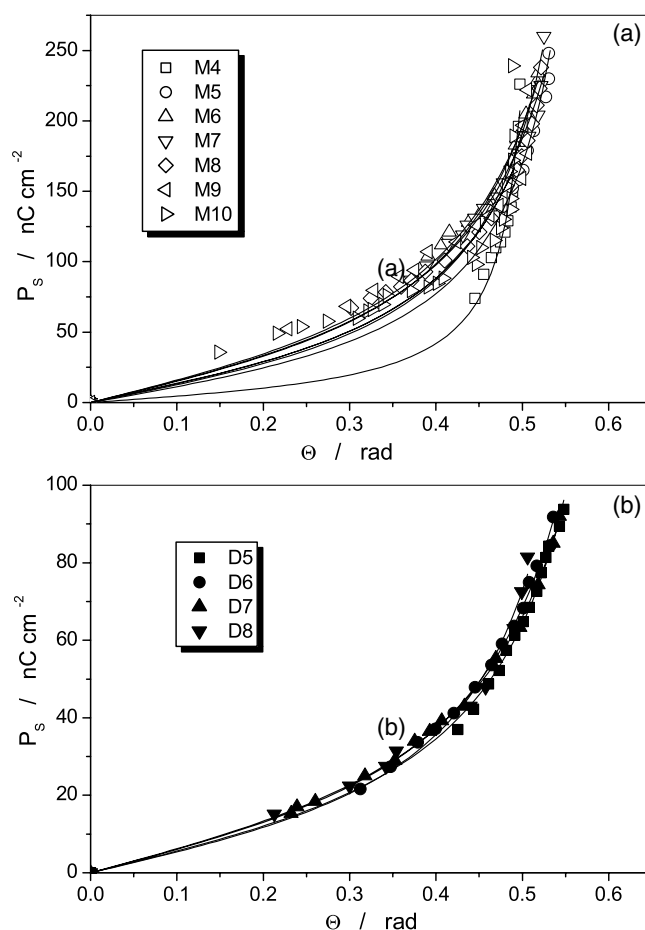


Figure 3. The dependence of the spontaneous polarization P_S on tilt angle θ for (a) the M-series and (b) the D-series of homologous compounds, as indicated in the legends of the graphs. The solid curves represent the least-squares fits according to equation (4).

temperatures (figure 1(b)). A similar temperature behaviour of $P_S(T)$ and $\theta(T)$ is observed for the D-series, as depicted in figure 2(a) and (b), respectively (the lines are a guide to the eye). Different homologues are indicated by full symbols according to the figure legends. Again, the temperature dependences are typical for SmC* behaviour, while we note that the tilt angle does not reach the kind of saturation as is observed for the M-series, which is due to the smaller temperature range of SmC* phase existence of the D-series. At reduced temperatures $T_C - T$ (≈ 30 K for the M-series and ≈ 10 K for the D-series), before the transition to the higher ordered phases but in both cases considerably below the phase transition into the SmC* phase, the spontaneous polarization P_S decreases linearly with increasing alkyl chain length n for both homologous series. This can be accounted for by an increased rotational freedom of the longer molecules and a decreased dipole moment per unit volume, both factors leading to a reduction of P_S . In contrast, at the same reduced temperatures $T_C - T$ the tilt angle θ is practically constant and independent of the molecular length, i.e. of chain length n , for both series under investigation. This is due to the fact that optical experiments detect the mesogenic core and x-ray experiments the electron density, both not being considerably modified by the addition

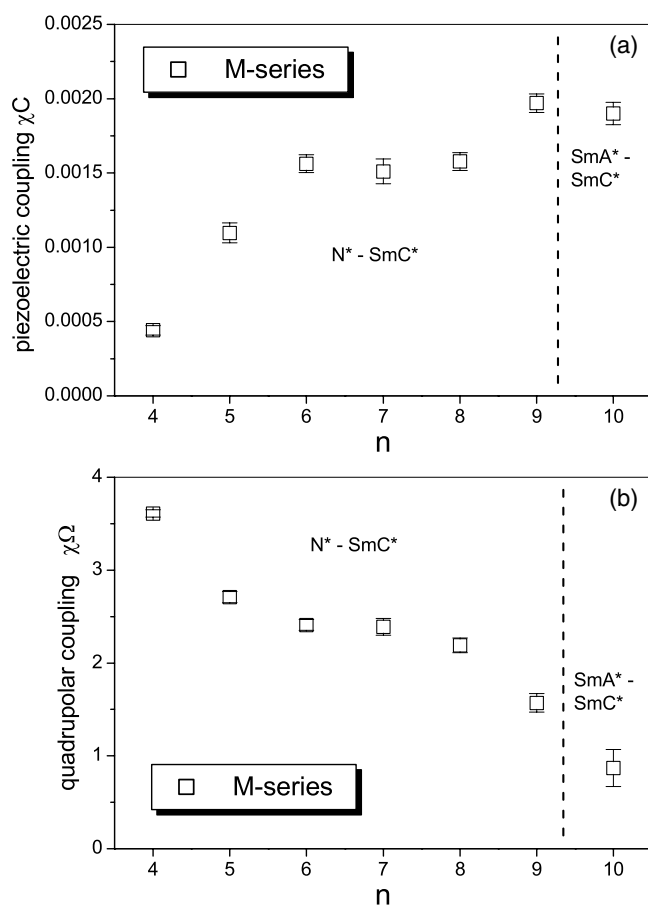


Figure 4. (a) Linear piezoelectric χC and (b) nonlinear quadrupolar $\chi\Omega$ contributions towards the polarization–tilt coupling as determined for the M-series of ferroelectric liquid crystals. This homologous series shows an abrupt change in the phase sequence from $N^* - SmC^*$ (M4–M9) to $SmA^* - SmC^*$ (M10).

of alkyl groups in the end-standing flexible chains. This behaviour may be somewhat obscured in figure 1 (M-series) by the larger variation in transition temperatures and the ‘discontinuous’ crossover from an $N^* - SmC^*$ to an $SmA^* - SmC^*$ transition for increasing alkyl chain length, as compared to the more ‘smooth’ evolution of the phase transition via a mediating twist grain boundary (TGBA *) phase in the D-series (figure 2).

Figure 3 shows the dependence of the spontaneous polarization P_S on tilt angle θ for temperatures well below the respective phase transition temperatures ((a) for the M-series and (b) for the D-series). It is evident for both homologous series that the behaviour is nonlinear at lower temperatures, i.e. larger tilt angles and larger spontaneous polarization, as also observed in other investigations [10, 11]. The solid curves in figures 3(a) and (b) represent least squares fits of the data to equation (4), with the two fit parameters χC and $\chi\Omega$ representing the linear (piezoelectric) and nonlinear (quadrupolar) contributions to the polarization–tilt coupling, respectively. While for the M-series (figure 3(a)) the polarization–tilt coupling changes quite considerably, especially for the short chain members of the homologous series, changes are much less pronounced for the homologues of the D-series

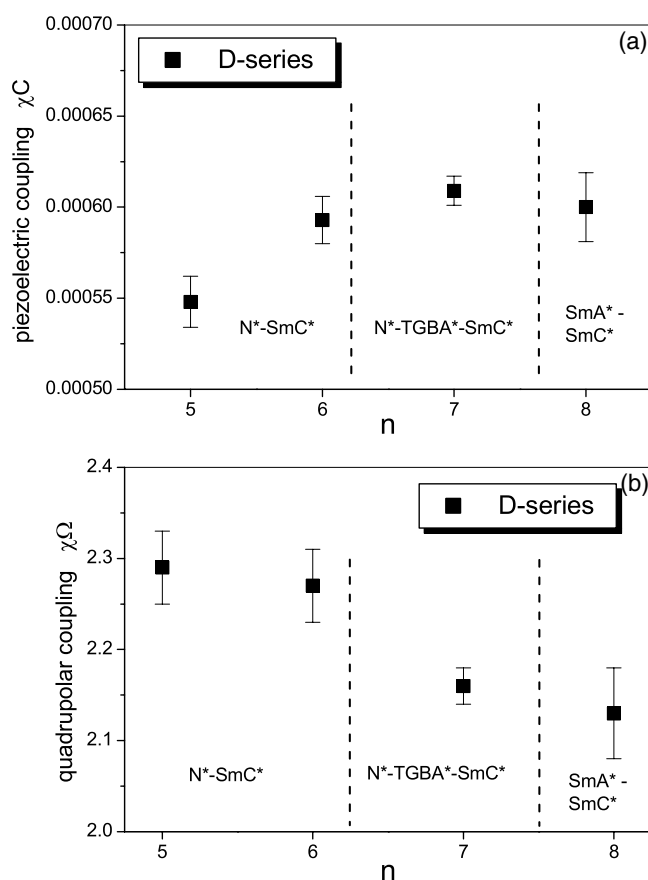


Figure 5. (a) Linear piezoelectric χ_C and (b) nonlinear quadrupolar χ_Ω contributions towards the polarization-tilt coupling as determined for the D-series of ferroelectric liquid crystals. This homologous series shows a 'continuous' change in the phase sequence from N^* -SmC* (D5, D6) via N^* -TGBA*-SmC* (D7) to SmA*-SmC* (D8).

(figure 3(b)). We attribute this behaviour to the differences in phase sequence of the two series. The M-series exhibits an N^* -SmC* transition for most of its members investigated, only showing a narrow SmA* phase for M10. It is thus likely that increasing the alkyl chain length changes the transition into SmC* from strongly first order (M4, M5) to second order (M10). The D-series on the other hand exhibits a 'smoothly' changing phase sequence from N^* -SmC* (D5, D6) to SmA*-SmC* (D8) via the incorporation of a frustrated twist grain boundary TGBA* phase (D7). The transition into SmC* is here presumably 'smoothly' varied from weakly first order to second order on increasing chain length, as evidenced by the only very small changes in the polarization-tilt coupling. This is exemplified by the variation of the respective χ_Ω -coupling contributions obtained for both series, changing by a factor of 5 from M4 to M10 and only by a factor of 1.2 from D5 to D8. (Values are given in arbitrary units, as we do not know the value of χ ; nevertheless we can discuss their general behaviour on increasing molecular length.) The respective contributions are shown in figure 4 for the M-series and in figure 5 for the D-series, both as a function of molecular length, i.e. for increasing number of carbon atoms in the achiral alkoxy chain, n . For the M-series the linear polarization-tilt coupling contribution increases with increasing molecular length, reaching

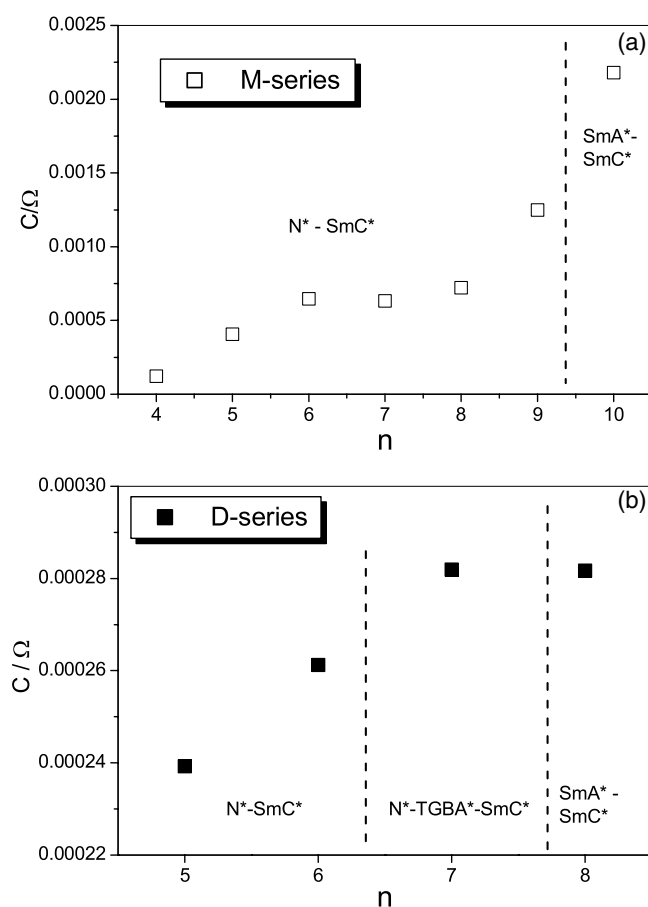


Figure 6. The ratio between the piezoelectric and the quadrupolar coupling constant for (a) the M-series and (b) the D-series of homologous ferroelectric liquid crystal materials.

saturation for longer molecules (figure 4(a)). Similarly, the nonlinear quadrupolar contribution to the polarization–tilt coupling decreases with increasing molecular length (figure 4(b)). A somewhat discontinuous behaviour seems to be observed as the phase sequence changes from N*–SmC* to SmA*–SmC* ($n = 10$).

For the D-series the phase sequence changes from N*–SmC* (D5, D6) via N*–TGBA*–SmC* (D7) to N*–TGBA*–SmA*–SmC* (D8) for increasing molecular length, i.e. increasing number of carbon atoms in the achiral alkoxy-chain, n . Note that the molecular structure of the D-series is very similar to that of the M-series. The chiral flexible group is the same; so is the achiral flexible group. The only difference in molecular structure lies in the CH₂–CH₂ linking-group within the D-series mesogenic core, which is missing for the compounds of the M-series. This accounts for the lower spontaneous polarization of the D-series as compared to that of the M-series, due to increased molecular flexibility. Thus also the chiral piezoelectric coupling contribution χC is reduced when comparing the D- to the M-series. The non-chiral coupling contribution $\chi \Omega$ on the other hand is of the same order of magnitude. For the D-series homologues the linear (piezoelectric) polarization–tilt coupling contribution increases smoothly into saturation as the phase sequence varies ‘continuously’ by incorporating a twist grain boundary TGBA* phase for increasing molecular length (figure 5(a)). At the same time

the nonlinear (quadrupolar) polarization–tilt coupling contribution decreases smoothly with increasing molecular length (figure 5(b)).

Without knowledge of the numerical value of the dielectric susceptibility χ we restrict the discussion to the ratio between linear and nonlinear contributions to the polarization–tilt coupling, i.e. to the ratio between the piezoelectric coefficient and the quadrupolar coupling constant, C/Ω . The respective data are depicted in figure 6(a) for the M-series and in figure 6(b) for the D-series. In the former case an increase of C/Ω is observed until saturation within the N*–SmC* phase sequence regime, while C/Ω strongly increases as the SmA*–SmC* transition is encountered for the M10 compound (figure 6(a)). In contrast, the compounds of the D-series, which exhibit phase sequences via TGBA* phases, exhibit smoothly increasing C/Ω values until saturation for increasing chain lengths (figure 6(b)).

4. Conclusions

We have investigated the polarization–tilt coupling of two homologous series of ferroelectric liquid crystals within the framework of the generalized Landau theory, i.e. with respect to linear piezoelectric and nonlinear quadrupolar contributions. The two homologues series investigated consist of molecules of very similar constitution, but varying phase sequence. It was found that the linear polarization–tilt coupling contribution increases with increasing length of the achiral flexible chain, approaching saturation for long chains, while the nonlinear, quadrupolar contribution decreases. For the homologous series with an abruptly changing phase sequence from N*–SmC* to SmA*–SmC* (M-series), there is evidence for a discontinuous change in the piezoelectric and quadrupolar coupling constants, while the homologous series incorporating twist grain boundary phases (D-series) exhibits a smooth development of the respective parameters.

References

- [1] Lagerwall S T 1999 *Ferroelectric and Antiferroelectric Liquid Crystals* (Weinheim: Wiley–VCH)
- [2] Musevic I, Blinc R and Zeks B 2000 *The Physics of Ferroelectric and Antiferroelectric Liquid Crystals* (Singapore: World Scientific)
- [3] Meyer R B, Liebert L, Strzelecki L and Keller P 1975 *J. Phys. Lett.* **36** L69
- [4] For an overview on ‘banana phases’ of bent-core molecules see: Pelzl G, Diele S and Weissflog W 1999 *Adv. Mater.* **11** 707
- [5] Huang C C and Viner J M 1982 *Phys. Rev. A* **25** 3385
- [6] Birgenau R J, Garland C W, Kortan A R, Lister J D, Meichle M, Ocko B M, Rosenblatt C, Yu L J and Goodby J W 1983 *Phys. Rev. A* **27** 1251
- [7] Indenbom V L, Pikin S A and Loginov E B 1976 *Sov. Phys.—Crystallogr.* **21** 632
- [8] Clark N A and Lagerwall S T 1980 *Appl. Phys. Lett.* **36** 899
- [9] Garoff S and Meyer R B 1977 *Phys. Rev. Lett.* **38** 848
- [10] Gießelmann F and Zugenmaier P 1995 *Phys. Rev. E* **52** 1762
- [11] Schacht J, Baethge H, Gießelmann F and Zugenmaier P 1998 *J. Mater. Chem.* **8** 603
- [12] Zeks B 1984 *Mol. Cryst. Liq. Cryst.* **114** 259
- [13] Carlsson T, Zeks B, Levstik A, Filipic C, Levstik I and Blinc R 1987 *Phys. Rev. A* **36** 1484
- [14] Mohr K, Köhler S, Worm K, Pelzl G, Diele S, Zschke H, Demus D, Andersson G, Dahl I, Lagerwall S T, Skarp K and Stebler B 1987 *Mol. Cryst. Liq. Cryst.* **146** 151
- [15] Schacht J, Dierking I, Gießelmann F, Mohr K, Zschke H, Kuczynski W and Zugenmaier P 1995 *Liq. Cryst.* **19** 151
- [16] Dierking I, Gießelmann F and Zugenmaier P 1994 *Liq. Cryst.* **17** 17
- [17] Dierking I, Gießelmann F, Kußerow J and Zugenmaier P 1994 *Liq. Cryst.* **17** 243
- [18] Miyasato K, Abe S, Takezoe H, Fukuda A and Kuze E 1983 *Japan. J. Appl. Phys.* **22** L661
- [19] Bahr Ch and Heppke G 1987 *Liq. Cryst.* **2** 825