Influence of an electric field on phase transitions in ferroelectric liquid crystals

Ch. Bahr[a]; G. Heppke[a]; B. Sabaschus[a]

[a] Iwan-N.-Stranski-Institute for Physical and Theoretical Chemistry, Technical University of Berlin, Berlin, Germany

PLEASE SCROLL DOWN FOR ARTICLE

Influence of an electric field
on phase transitions in ferroelectric liquid crystals

by CH. BAHR*, G. HEPPKE and B. SABASCHUS

Iwan-N.-Stranski-Institute for Physical and Theoretical Chemistry,
Technical University of Berlin, D-1000 Berlin 12, Germany

The transition temperatures between various smectic liquid crystal phases in chiral (ferroelectric) compounds have been determined as a function of an applied DC electric field. We find that S_G–S_A and S_G–S_C transitions show a field-induced temperature shift proportional to the applied field strength similar to the already known behaviour of first order S_C–S_A transitions. In contrast, for the non-ferroelectric S_B–S_A and S_E–S_B transitions no effect of the electric field is observed. The field-induced temperature shift is compared with the temperature shift occurring in chiral-racemic systems of the same compounds (see BAHR, CH., HEPPKE, G., and SABASCHUS, B., 1991, *Liq. Crystals*, 9, 31). Using Landau theory we derive a simple relation between these two quantities.

1. Introduction

Smectic liquid crystals show a large variety of different phases because of the various kinds of in-plane molecular order (ranging from liquid-like to long range positional ordering). The different phase types can be further divided into so-called orthogonal and tilted phases. In the orthogonal phases the director, i.e. the average direction of the long molecular axes, is parallel to the normal to the smectic layer planes, whereas in the tilted phases the director is inclined by a tilt angle with respect to the layer normal.

In 1975, Meyer *et al.* [1] showed that the tilted smectic phases possess a spontaneous electric polarization, P_s, if the molecules possess a permanent transverse dipole and are chiral. In the corresponding racemate P_s is zero and by mixing the chiral compound with its own racemate P_s can be continuously varied without changing most of the other physical properties. Recently, we have studied [2] the behaviour of various smectic phase transitions in such binary chiral-racemic systems. We have observed that transitions involving a tilted (and thus ferroelectric) phase occur in the chiral compound at slightly higher temperatures than in the racemate. As this effect is not observed for transitions between two orthogonal (non-ferroelectric) phases, we have concluded that the ferroelectric transition temperatures are shifted by the increasing amount of the spontaneous polarization in the chiral-racemic systems. A similar effect, i.e. a shift of the ferroelectric phase transition, is observed when an external electric field is applied. This behaviour has long been known for solid-state ferroelectrics [3] and was also studied in detail [4–6] for one type of liquid crystal ferroelectric phase transition, namely a first order [7] S_C–S_A transition.

Thus, a certain analogy exists between the shift of the transition temperature induced by an external electric field and the shift induced by the spontaneous

* Author for correspondence.

polarization which can be considered to act like an internal electric field. In the present study, we have investigated the influence of an external electric field on the chiral (ferroelectric) versions of the same liquid crystal compounds which were studied previously [2] in binary chiral-racemic systems. The compounds show a number of different orthogonal (S_E, S_B, S_A) as well as tilted phases (S_G, S_C). As expected, we find that the transitions involving a ferroelectric phase (S_C–S_A, S_G–S_A, S_G–S_C) show a significant shift of transition temperature in the presence of an electric field whereas the transitions between two non-ferroelectric phases (S_B–S_A, S_E–S_B) are not influenced by an electric field. The field-induced shift of the S_G–S_A and the S_G–S_C transitions is described here, to our knowledge, for the first time.

2. Experimental

The structures and the transition temperatures of the three liquid crystal compounds (labelled as A7, A6 and B5), which were studied previously in chiral-racemic systems, are given in table 1. For comparison, a fourth compound (C7) is included, whose behaviour in an external electric field has already been studied in detail [5, 6]. The compounds, in their isotropic phase, were filled into conductively coated glass cells (thickness 9 μm) with planar orienting surfaces allowing the application of an electric field along the smectic layer planes (i.e. parallel to the direction of the spontaneous polarization of the ferroelectric phases). The cells were placed into a temperature controlled oven which allowed optical observation of the samples. The field-induced shift of the transition temperatures was determined mainly by two methods. First, we have observed the sample through a polarizing microscope and detected the transition temperatures (indicated by the easily observable texture changes) for several values of the applied DC electric field. Secondly, we have measured the temperature dependence of the static dielectric constant ε of the sample which shows, at most of the transitions, a marked behaviour, for example, a discontinuous jump. For this purpose, we used a HP4274A LCR meter which measured continuously the capacitance of the sample cell for several values of an applied DC bias field while the temperature was changed at a slow constant rate ($0 \cdot 05$–$0 \cdot 1$ K min^{-1}). The details of this procedure are described in [6].

3. Results

Figure 1 shows the temperature dependence of the static dielectric constant ε near the S_G–S_A transition of the compound A6 at various applied bias fields. In the S_A phase, ε shows an increase with decreasing temperature corresponding to the usual electroclinic soft mode behaviour of the S_A phase of chiral molecules [8]. The phase transition to the S_G phase was observed as a sudden decrease of the ε values coinciding with the texture change observed simultaneously. As figure 1 demonstrates, the transition shifts to higher temperatures with increasing field strength and a linear relation between the induced temperature shift ΔT and the applied field strength E exists, i.e. ΔT is proportional to E (see figure 2). For the S_G–S_C transition in compound A7 the same behaviour is observed, the field-induced temperature shift being slightly larger than for the S_G–S_A transition (see figure 3). For the first order S_C–S_A transitions in compounds A7 and C7 the field-induced temperature shift has already been determined [4]. There is one difference between the S_C–S_A transitions and the other transitions under investigation; the line which separates the polarized S_A phase from the ferroelectric S_C phase in the T–E diagram terminates at a critical point where both phases become indistinguishable [6]. This is not the case for the S_G–S_A and S_G–S_C

Table 1. Molecular structure and phase sequences.

Compound	Structure
A7	$C_7H_{15}O$—◯—◯—OCO-$\underset{*}{CH}(Cl)$-$CH(CH_3)_2$
	S_G 71·2°C S_C^* 73·1°C S_A 81·7°C I
A6	$C_6H_{13}O$—◯—◯—OCO-$\underset{*}{CH}(Cl)$-$CH(CH_3)_2$
	S_G 77·6°C S_A 83·3°C I
B5	$C_5H_{11}O$—◯—◯—OCO-$\underset{*}{CH}(Cl)$-CH_2-$CH(CH_3)_2$
	S_E 62·9°C $S_{B_{cryst}}$ 71·3°C S_A 74·5°C I
C7	$C_7H_{15}O$—◯—◯—OCO-$\underset{*}{CH}(Cl)$-$\underset{*}{CH}(CH_3)$-C_2H_5
	S_C^* 55·0°C S_A 62°C I
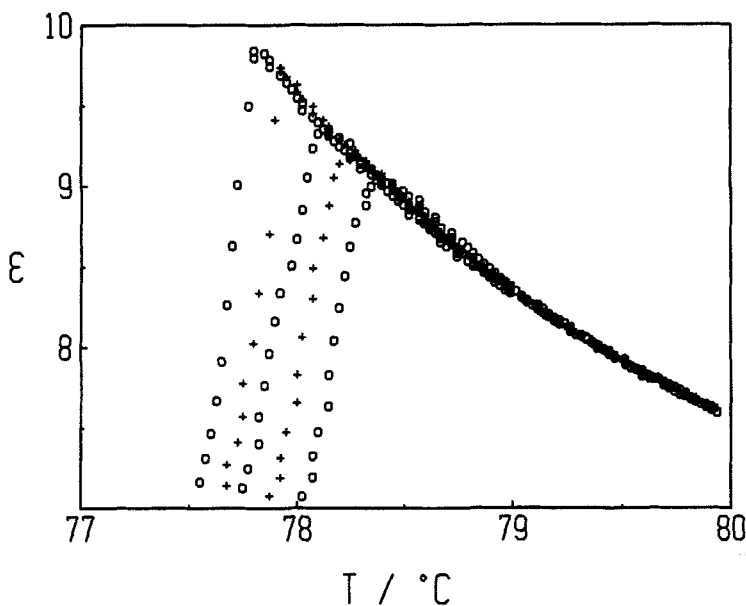
Figure 1. Temperature dependence of the static dielectric constant ε near the S_G–S_A transition of compound A6. The curves are recorded at bias field strengths of 0 (left hand curve), 17, 33, 50, and 67 kV cm^{-1} (right hand curve).

transitions which persist up to the limit of experimentally applicable field strengths (80–100 kV cm^{-1}).

Compound B5 exhibits only the non-ferroelectric phases S_A, S_B, and S_E. The transitions between these phases are not affected by the application of an electric field, as is demonstrated in figure 4 which shows the temperature dependence of the static

Ch. Bahr *et al.*
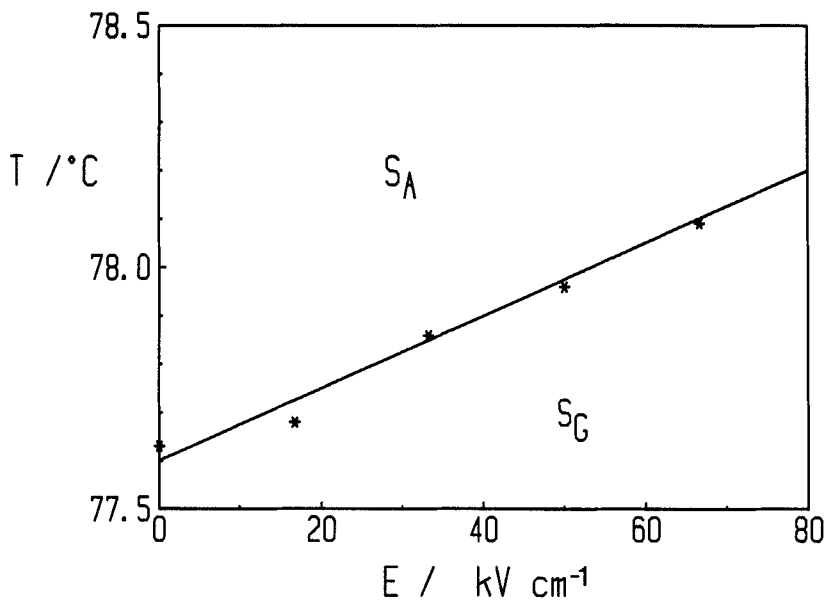
Figure 2. Electric field strength dependence of the S_G–S_A transition temperature of compound A6. (The designation S_A for the high temperature phase is, in a strict sense, not correct because the electric field induces a tilt angle resulting in a structure corresponding to a S_C phase. Thus, the orthogonal S_A phase exists only in zero field).
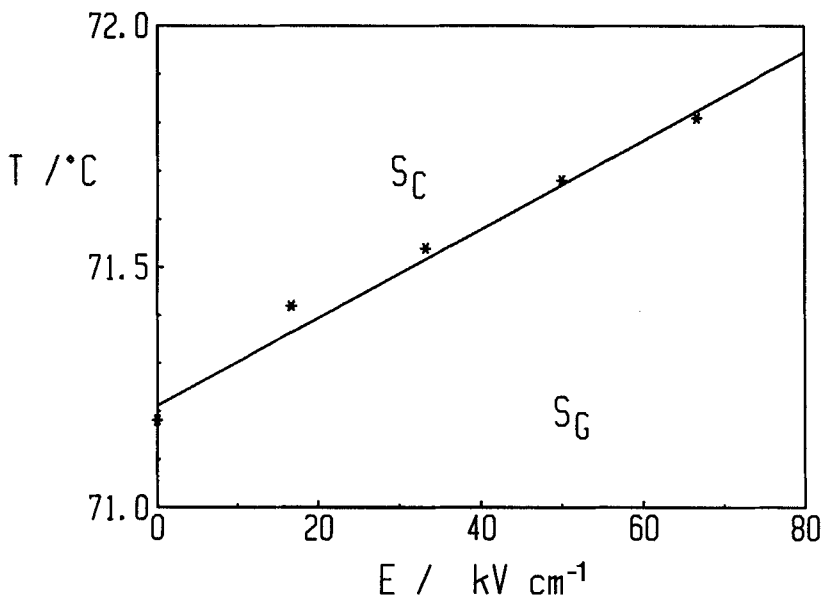

Figure 3. Electric field strength dependence of the S_G–S_C transition temperature for compound A7.

dielectric constant ε near the S_B–S_A transition. At this transition ε shows a distinct increase because of the larger electroclinic effect in the S_B phase [9]. The two curves shown in figure 4 were recorded under a bias field of 0 and $67\,kV\,cm^{-1}$. Within our experimental resolution, no effect of the electric field could be observed [10].

Summarizing our experimental results we find a field-induced temperature shift for all transitions involving a ferroelectric phase whereas transitions between two non-ferroelectric phases are not affected by the electric field. The situation is completely analogous to the behaviour of these phase transitions in chiral-racemic systems [2]. In table 2 we have listed the quantitative values of the field-induced temperature shifts, $\Delta T/E$, together with the temperature difference $T_{chi} - T_{rac}$ observed in the binary chiral-racemic systems. The value of $T_{chi} - T_{rac}$ for compound C7 is somewhat uncertain because its racemate is not, as for the other compounds, prepared by mixing the two antipodes showing almost identical transition temperatures. Instead we had to prepare the C7 racemate by a separate synthesis starting from a commercially available *DL*-isoleucin containing about 10 per cent alloisoleucine; thus the observed temperature difference to the chiral C7 may be partly affected by the presence of some impurities.

At first sight there is no obvious relation between the values of $\Delta T/E$ and $T_{chi} - T_{rac}$ given in table 2. However, regarding the values of the transition entropy density ΔS of the various phase transitions, determined by DSC measurements, there seems to be a tendency that $\Delta T/E$ becomes large for small values of ΔS whereas the values of $T_{chi} - T_{rac}$ are less influenced by ΔS. (The values of ΔS given in table 2 are calculated assuming a density of $1\,g/cm^3$.) In the following we show that a simple Landau model predicts a certain relation between the electric field-induced temperature shift determined in the chiral compounds and the temperature shift observed in the chiral-racemic systems, namely a constant value of the ratio $(\Delta T/E)/[(T_{chi} - T_{rac})/\Delta S]^{1/2}$, regardless of the type of transition.

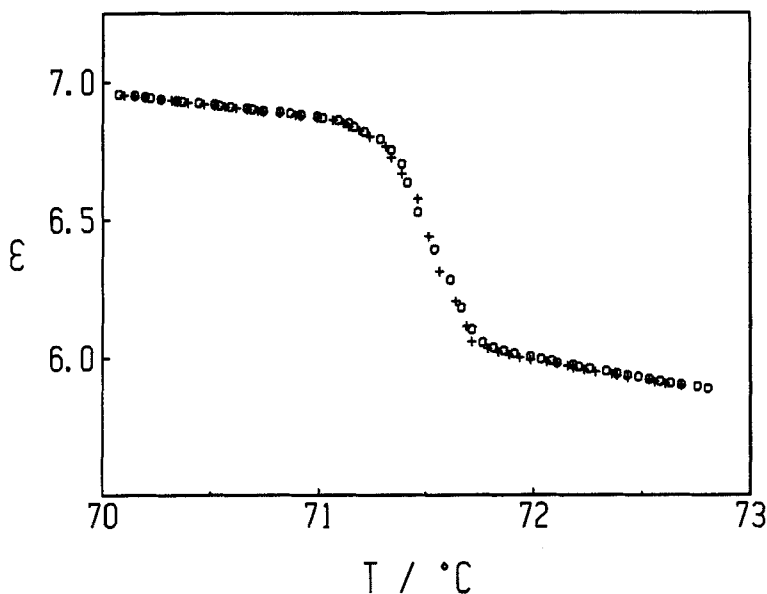Figure 4. Temperature dependence of the static dielectric constant ε near the S_B–S_A transition of compound B5. The two curves are recorded at bias field strengths of 0 (+) and $67\,kV\,cm^{-1}$ (○).

Table 2.   A comparison between $\Delta T/E$ and $T_{\text{chi}} - T_{\text{rac}}$.

Compound	Transition	$\dfrac{\Delta T/E}{10^{-8}\,\text{kV}^{-1}\,\text{m}}$	$\dfrac{T_{\text{chi}} - T_{\text{rac}}}{\text{K}}$	$\dfrac{\Delta S}{10^{3}\,\text{J}\,\text{m}^{-3}\,\text{K}^{-1}}$	$\dfrac{(\Delta T/E)/[T_{\text{chi}} - T_{\text{rac}}]/\Delta S]^{1/2}}{10^{-6}\,\text{C}^{1/2}\,\text{V}^{-1/2}\,\text{m}^{-1/2}}$
A7	S_C–S_A	24	0·8	3·5	16
A7	S_G–S_C	10	1·0	32	18
A6	S_G–S_A	8	1·0	40	16
C7	S_C–S_A	20	≈ 2	5·5	11
B5	S_B–S_A	0	0	18	—
B5	S_E–S_B	0	0	11	—

We consider the simplest Landau free energy expression for a first order transition of an improper ferroelectric with a bilinear coupling between the order parameter and polarization [11]

$$g = \tfrac{1}{2}a(T - T_0)\theta^2 + \tfrac{1}{4}b\theta^4 + \tfrac{1}{6}c\theta^6 + \frac{1}{2\chi_0\varepsilon_0}P^2 - CP\theta. \tag{1}$$

Here, θ denotes the order parameter of the transition, P is the polarization, C is the bilinear $P - \theta$ coupling constant, χ_0 is the electric susceptibility at fixed θ and ε_0 is the vacuum permittivity. With a, $c > 0$ and $b < 0$ equation (1) describes a first order transition between a high temperature phase with $\theta = 0$ and a low temperature phase with $\theta > 0$. In the low temperature phase a polarization P appears additionally which is linearly coupled to the order parameter θ as $P = C\chi_0\varepsilon_0\theta$. For the S_C–S_A transition θ is given by the tilt of the director with respect to the layer normal and we have recently shown [6] that a first order S_C–S_A transition and its behaviour in an external field is well described by this simple Landau model. Here, we assume that the S_G–S_A and S_G–S_C transitions can also be described by equation (1) provided that the order parameter θ is defined in a suitable way. For the following considerations it is, however, not necessary to identify θ with certain physical properties of our liquid crystals, if we accept the assumption that for the S_G–S_A and S_G–S_C transitions the polarization is also coupled linearly (to a first approximation) to the chosen order parameter of the transition (in the case of the S_G–S_C transition, P in equation (1) does not correspond to the total spontaneous polarization of both phases but only to that part of the polarization which appears additionally in the S_G phase).

Within the framework of our Landau model, the first order transition temperature of the chiral ferroelectric compounds is given by

$$T_{\text{chi}} = T_0 + \frac{3b^2}{16ac} + \frac{C^2\chi_0\varepsilon_0}{a}. \tag{2}$$

In the racemic non-ferroelectric versions of the compounds the coupling constant C is zero, i.e.

$$T_{\text{rac}} = T_0 + 3b^2/(16ac),$$

and we find for the transition temperature difference between the chiral compound and its racemate

$$T_{\text{chi}} - T_{\text{rac}} = \frac{C^2\chi_0\varepsilon_0}{a}. \tag{3}$$

The electric field-induced temperature shift $\Delta T/E$ which we observe for the chiral compounds can be described by a Clausius–Clapeyron type of equation [12]

$$\frac{\Delta T}{E} = \frac{\Delta P}{\Delta S}. \tag{4}$$

For the S_C–S_A transitions in C7 and A7 there is good agreement between the experimental values of $\Delta T/E$ and the values calculated by equation (4) [4]. For the S_G–S_A and S_G–S_C transitions we cannot check equation (4) because the viscosity in the S_G phase of our compounds is too large to measure P_s by the conventional methods. If we calculate ΔP according to equation (4) using the values of $\Delta T/E$ and ΔS given in table 2 we find that ΔP should amount to 310 (S_G–S_C) and 460 nC/cm^2 (S_G–S_A) which are reasonable values [13]. We assume therefore that equation (4) also holds for these transitions and express the quantities ΔP and ΔS within the framework of the Landau model. The jump of θ at the first order transition is given by

$$\Delta\theta = \left(-\frac{3b}{4c}\right)^{1/2}. \tag{5}$$

Then, we find for ΔP

$$\Delta P = C\chi_0\varepsilon_0\left(-\frac{3b}{4c}\right)^{1/2}. \tag{6}$$

Calculating the entropy as $S = -\partial g/\partial T = -\frac{1}{2}a\theta^2$ we find

$$\Delta S = \frac{3ab}{8c}. \tag{7}$$

Thus, equation (4) can be rewritten as

$$\frac{\Delta T}{E} = \frac{4C\chi_0\varepsilon_0}{a}\left(-\frac{c}{3b}\right)^{1/2}, \tag{8}$$

and in combination with equation (3) we finally obtain

$$\frac{\Delta T}{E} = \left[2\chi_0\varepsilon_0\frac{(T_{chi}-T_{rac})}{\Delta S}\right]^{1/2}. \tag{9}$$

Since the susceptibility χ_0 can be assumed to vary only very slightly for our different compounds, this simple model predicts an almost constant value of the ratio $(\Delta T/E)/[(T_{chi}-T_{rac})/\Delta S]^{1/2}$. The experimental values of this ratio are given in table 2. Although the values are far from being constant they are within a relatively narrow range between 11 and 18×10^{-6} C$^{1/2}$ V$^{-1/2}$ m$^{-1/2}$. On the other hand, all of the experimental values are clearly larger than the theoretically predicted value of $(2\chi_0\varepsilon_0)^{1/2}$ (cf. equation (9)) which amounts to $8.4 - 9.4 \times 10^{-6}$ C$^{1/2}$ V$^{-1/2}$ m$^{-1/2}$ for $\chi_0 = 4 - 5$. Thus, equation (9) seems to be a fair first approximation which predicts the right order of magnitude for the transition temperature shifts of the ferroelectric liquid crystals studied.

In conclusion, we have shown that, as known for first order S_C–S_A transitions, S_G–S_A and S_G–S_C transitions in chiral liquid crystal compounds are also shifted to higher temperatures by the application of an external electric field whereas the S_B–S_A and S_E–S_B transitions in a similar chiral compound are not influenced by the electric field. The situation is completely analogous to the behaviour

of these transitions in binary chiral-racemic systems where only the transitions involving a tilted phase show a temperature shift to higher values with increasing chirality. We have shown that a simple Landau model, based on a linear coupling between polarization and order parameter, predicts a certain relation between the field-induced temperature shift $\Delta T/E$ and the temperature difference between chiral and racemic compounds $T_{\text{chi}} - T_{\text{rac}}$. Our experimental results confirm, to a first approximation, our theoretical considerations. Thus, the study presented here is a further confirmation for the conclusion of our previous investigation [2], namely that the temperature shift in chiral-racemic systems can be considered as a result of the internal electric field caused by the spontaneous polarization.

References

[1] MEYER, R. B., LIEBERT, L., STRZELECKI, L., and KELLER, P., 1975, *J. Phys. Lett., Paris*, **36**, L69.

[2] BAHR, CH., HEPPKE, G., and SABASCHUS, B., 1991, *Liq. Crystals*, **9**, 31.

[3] MERZ, W. J., 1953, *Phys. Rev.*, **91**, 513.

[4] BAHR, CH., and HEPPKE, G., 1987, *Molec. Crystals liq. Crystals*, (b), **150**, 313.

[5] BAHR, CH., and HEPPKE, G., 1989, *Phys. Rev. A*, **39**, 5459.

[6] BAHR, CH., and HEPPKE, G., 1990, *Phys. Rev. A*, **41**, 4335.

[7] S_C–S_A transitions are either first order or, in the vast majority of cases, second order. However, because the electric field induces a tilt in the S_A phase, only the first order transition persists in the presence of an electric field; in the second order case, the situation in the presence of an electric field is comparable to that of a liquid–gas system in the supercritical region.

[8] GAROFF, S., and MEYER, R. B., 1977, *Phys. Rev. Lett.*, **38**, 848.

[9] BAHR, CH., and HEPPKE, G., 1988, *Phys. Rev. A*, **37**, 3179.

[10] In principle, there should also be in this case a temperature shift. Because of the larger ε value the S_B phase gains in the presence of an electric field a free energy decrease corresponding to $\Delta\varepsilon E^2$ compared to the S_A phase ($\Delta\varepsilon$ being the ε difference between the two phases). However, we can estimate that this shift is negligible for experimentally reasonable field strengths.

[11] LINES, M. E., and GLASS, A. M., 1977, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon Press), p. 353.

[12] LINES, M. E., and GLASS, A. M., 1977, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon Press), p. 169.

[13] Similar ferroelectric liquid crystal compounds possessing the same chiral groups but three aromatic rings show S_J phases (which possess a structure very similar to S_G phases) in which P_s can be measured. The corresponding values are in the range of 300–$600\,\text{nC/cm}^2$ (LÖTZSCH, D. private communication).