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Ferroelectric Liquid Crystals with High Spontaneous Polarization

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1. Introduction

Liquid crystalline (LC) materials are example of self-assembling media on a nanoscale level (de Gennes & Prost, 1993; Gray, 1987; Lagerwall, 1999). Composed of anisotropic molecules, LC compounds exhibit a great variability of structures, which are strongly susceptible to external fields as well as to interaction with the surfaces. For particular molecules assembled in specific architectures a permanent dipole moment can appear thus forming structures with dipolar order, namely ferroelectric (FE) or antiferroelectric (AF) phases. Their physical properties have been intensively investigated, as they promised large variety of applications, e.g. in displays, displays with a memory, TV screens, spatial light modulators, applications in optical processing, computing, etc. (Clark & Lagerwall, 1983; Goodby et al., 1991; Lueder, 2010; Yang & Wu, 2006). Recently, also a display based on AF SmC* materials has been reported, profiting from their higher threshold electric field for switching (Lagerwall, 1999). The application potentialities stimulated a great progress in the synthesis and research of these materials.

The outstanding physical properties of the FE (and possibly AF) smectic LCs (SmC*) are attracting attention especially after the nematic liquid crystal materials have been developed to the limits of their performance.

The chapter is structured as follows. In the first part, we recall the main structural characteristics of LC molecules and their assembling in liquid crystalline phases, with stress to formation of FE phases. The origin of the spontaneous polarization from the molecular structure and supramolecular alignment is described.

The value of spontaneous polarization is a main characteristic of ferroelectric liquid crystals (FLC) and it is also an important parameter considered when selecting a material for specific applications. Therefore, designing the molecular structure with the aim to influence and particularly enhance the spontaneous polarization value of the resulting ferroelectric phase is the principal goal of the second part of this contribution. In particular, we discuss influence of molecular and intramolecular rotations, an asymmetry of the chiral centre, transversal molecular dipole moments, the presence of polar groups in the chiral centre, the lateral substitutions, the presence of heteroaromatic rings in the central skeleton of the molecule, etc. One paragraph concerns ferroelectric mixtures, as in any application of FLC, as well as of any LCs, mixtures of several compounds are used with optimized properties.
Finally, a brief survey of a new type of liquid crystalline materials is devoted to polar liquid crystals composed of non-chiral bent-core molecules (so called banana liquid crystals), which may exhibit AF phases and quite exceptionally FE phases. In both cases their spontaneous polarization is high.

2. Liquid crystalline phases

Liquid crystals are partially ordered anisotropic fluids, thermodynamically located between the three-dimensionally ordered solid state (crystal) and the isotropic liquid. They may flow like a liquid, but their molecules may be oriented in a crystal-like way. Typical constituents of liquid crystals are elongated rod-like organic molecules (de Genes & Prost, 1999; Gray, 1987) the ratio between the length and the diameter of such molecules being about 5 or larger. Due to fast thermal rotation (of the order of $10^{-9}$ s) around the long molecular axis they can be regarded as a cylinder. The molecules consist of rigid core with two or more aromatic rings with a flexible linear terminal substituents. Polar substituents are needed if electro-optic behavior is expected. With balanced rigid and flexible parts of molecules, the compound exhibits liquid crystalline phases (mesophases).

Besides the positional order typical for the solid state, the molecules with strongly anisotropic form may also possess orientational order. There are many types of mesophases differing in the type and range of both orientational and positional order. These phases can be distinguished by their physical properties, which exhibit specific anisotropy reflecting the phase symmetry.

2.1 Ferroelectric liquid crystalline phases

An idea of the ferroelectric mesophase was presented by R.B. Meyer at the 5th International Liquid Crystal Conference in 1974. From symmetry considerations the author deduced that all tilted smectic phases composed of chiral molecules (without mirror symmetry) have to exhibit a (local) spontaneous polarization if the molecules contain a transverse permanent dipole moment.

The first synthesized compound fulfilling Meyer’s specification is known by an acronym DOBAMBC, standing for (S)-(-)-p’-decyloxybenzylidene p’-amino 2-methylbutyl cinnamate (Meyer et al., 1975). The molecule of DOBAMBC contains an asymmetric carbon atom C’ rendering molecular chirality, while a lateral --C = O group provides a transverse permanent dipole moment $p_t$. The aliphatic chain attached to the other end of the molecule by an oxygen atom is relatively long, favoring the SmC mesophase. In this phase molecules are arranged in fluid layers with no long-range translational order that can slide one over the other. On average, molecules are tilted from the layer normal by an angle $\theta$. The phase is optically biaxial. For review of basic properties of ferroelectric liquid crystals see (Goodby et al., 1991, Kitzerow & Bahr, 2001). The molecular structure of the chiral smectic C mesophase (SmC*, star standing for chirality) is depicted in Fig. 1. Each layer is similar to that of the usual SmC phase, but because of
Fig. 1. The helicoidal structure of chiral smectic C (SmC*) liquid crystal. The molecular dipole moment $p_i$ is always perpendicular to the director $n$ and tangential to the circle of intersection of the cone with the boundary plane of the layer. Azimuthal angle $\phi$ is a function of the coordinate $z$ parallel to the layer normal, $\theta$ is the tilt angle.

Chirality there is a non-zero in-layer spontaneous dipole moment which is perpendicular to the average molecular direction (director $n$) and to the tilt direction. To understand the origin of the layer dipole moment one has to consider that in contrast to the non-chiral molecules, the chiral ones do not rotate freely along their long axes. The chiral centre represents a steric hindrance for the molecular rotation, which results in a non-compensated part of the transversal molecular dipole moment $p_i$. Due to random head-tail alignment of molecules only an in-layer component of the dipole moment remains, and create the layer dipole moment $P$.

The other aspect of chirality is rotation of the director and thus also of the direction of dipole moment $P$ about the smectic layer normal (see Fig. 1). The helix can be either right-handed or left-handed depending on the chirality of constituent molecules. Due to formation of the helical superstructure the spontaneous polarization is compensated to zero within one pitch of the helix, $p$, and the material appears to be non-polarized. Thus, strictly speaking, the SmC* phase is not ferroelectric, but use to be regarded as helielectric.
Under an external electric field the local polarization $P$ is aligned to the field direction thus unwinding the helical structure. In an alternating (a.c.) electric field a typical ferroelectric switching current, as well as electrooptical response is observed. This effect, being relatively fast (~10 $\mu$s), represents the main principle of technical applications.

From the switching current the value of the macroscopic spontaneous polarization, $P_s$, of the material can be evaluated.

To understand the origin of the layer dipole moment $P$ several models have been suggested. In very simple one (Beresnev & Blinov, 1981), the molecules are considered as being tilted within layers and randomly distributed head to tail (Fig. 2). The chiral centre is depicted as an uneven tripod with unequally long arms. From steric reason the molecules prefer to tilt in the direction shown in Fig. 2a rather than in Fig. 2b and all the transverse molecular dipoles lie preferentially in one direction, orthogonal to the tilt direction. In reality, the molecules are spinning rapidly, and this preferred tilt direction then becomes a more energetically favored position due to steric hindrance if an mirror symmetry is absent in the layer.

Fig. 2. Schematic arrangement of chiral molecules in the SmC* phase, $p_i$ being the molecular dipole moment. Due to chiral group, depicted by the tripod, the molecules prefer (a) rather than (b) and thus all the molecular dipole moments lie in the direction as shown in lower part of the figure as $P$.

For application of FLCs in electrooptical displays, the helicoidal structure must be suppressed otherwise an optically homogeneous field cannot be reached. It is achieved in so called Surface Stabilized Ferroelectric Liquid Crystal (SSFLC) being only about 1 $\mu$m thick (Clark & Lagerwall, 1983).

It is necessary to accent that in many FLCs the value of $P_s$ is considerably temperature dependent. With increasing temperature $P_s$ decreases and disappears at the transition to the high temperature SmA phase, chiral nematic phase (N*) or isotropic liquid at specific temperature $T_c$. Typical behavior of such temperature dependence is seen in Fig. 3.
Fig. 3. Temperature dependence of the spontaneous polarization for series of compounds XV for X = F; n, m are numbers of carbon atoms in aliphatic chains (see Tab. 8), $T_c$ is a temperature at which the SmC* phase transforms to a phase without spontaneous polarization.

In addition, temperature range of the SmC* phase strongly differs for various substances. Therefore, for comparison of the spontaneous polarization of different compounds values of $P_s$ at a definite temperature $T$ below $T_c$ use to be given (usually for $T_c - T = 5, 10$ or $20$ K). But still comparison of the spontaneous polarization for different substances at the same temperature is solitary.

Let us point out that both FE and AF dipolar order exists also in tilted chiral smectic phases, in which (in contrast to the SmC* phase) the smectic layers exhibit a hexatic molecular arrangement due to a strong bond orientational order, or in so called low temperature chiral tilted smectics with a hexagonal or square molecular arrangement within the smectic layers and long range correlations in the direction of the smectic layer normal. These types of phases are not suitable for application as the polarization switching as well as the electrooptic response is significantly slower or are not switchable at all.

3. Relation of the molecular structure and the SmC* phase formation

Basic requirements on molecules to be able to create the SmC* mesophase can be described as follows:

1. Rod-like shape and ability to form a layered mesophase where the long axes of constituent molecules are tilted with respect to the layer planes. In more detail see e.g. (Goodby et al., 1991).
2. Chirality (either right- or left-handed), ensured by the presence of at least one asymmetric carbon, located usually on one or on both ends of molecules. Location of the asymmetric carbon in the central part of molecule is very rare (Barbera et al., 1989).

3. The existence of a transversal dipole moment borne by a functional group e.g. -C=O, -CN, -Cl, etc. This dipole moment is not averaged to zero by the molecular rotation because of hindering by the chiral centre. As for the intramolecular motion, rotation between the polar and chiral groups is not free.

In the following discussion we limit oneself to substances containing asymmetrical carbon only in one side of molecule, since possibilities of practical use of materials with asymmetrical carbon on both ends and/or in the central core of a molecule are scarce. Only a few such substances are known to establish generally valid relations.

For the following consideration, it is advantageous to divide a typical rod-like FLC molecule to several parts:


- **a. Central linear rigid core** is formed as a rule by two or three aromatic or heteroaromatic rings denoted as \( A \), which are connected by linkage groups \( X \) and \( Y \). As a rule \( X \) and \( Y \) represent a simple bond, e.g. -COO-, -CH=N-, -N=N- etc.
- **b. Non-chiral terminal chain** \( R \) (as a rule an unbranched alkyl- or alkyloxy group).
- **c. Chiral terminal chain** \( R^* \) with one or more asymmetric carbons \( C^* \), most frequently it is -C*H(CH\( _3 \))-(CH\( _2 \))\( _m \)CH\( _3 \), \( m = 1 \) to 5.
- **d. Linkage group** \( Z \) between the core and the terminal chains formed either by a single bond or combination of more groups, some of them bringing the molecule transverse dipole moment (e.g. -CH\( _2 \)-, -CH=CH-, -COO-, -CO-).

Presently, number of substances composed of rod-like molecules and forming the ferroelectric mesophase amounts to thousands. Unfortunately, in many of them the values of \( P_s \) at temperatures relevant for comparison are not available. Therefore, evaluation of factors influencing \( P_s \) is rather difficult. The most promising ways for \( P_s \) increase are discussed below.

4. **Ways of spontaneous polarization enhancement**

For the value of the spontaneous polarization \( P_s \), the existence of the lateral molecular dipole moments \( p_l \) is essential and increasing of \( p_l \) seems to be the first natural way for \( P_s \) increasing. One has to realize that the \( P_s \) value is not just a result of a simple addition of \( p_l \) values in the volume. Rotation of LC molecules around their long axes and various intramolecular rotations lower this value significantly. Therefore, restriction of these rotations is further and very important way to \( P_s \) enhancement. Both ways closely relate to configuration of the chiral centre in the molecule, to number of asymmetric carbons in the molecule and are connected with nature of the bond between the chiral part and central linear rigid core. Therefore, still new substituents have been examined (see Table 1), which finally resulted in preparation of compounds with very high spontaneous polarization up to the order of \( 10^2 \) nC cm\(^{-2} \).

In all Tables hereafter substituents \( C_m H_{2m+1} \) and \( C_n H_{2n+1} \) are linear. Aromatic rings are bonded in positions 1,4.
Table 1. Examples of chiral substituents.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Dipole Moment</th>
<th>Molecular Alignment</th>
<th>Spontaneous Polarization</th>
</tr>
</thead>
<tbody>
<tr>
<td>-C(H(CH₃))-R</td>
<td>X=CH₃,F,Cl,Br,OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-C’F(CH₃)-COO-R</td>
<td>R = CₘH₂ₘ₊₁</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-C’H(CF₃)-CH₂-COO-R</td>
<td>R = CₘH₂ₘ₊₁</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-C’H(X)-C’H(CH₃)-R</td>
<td>X = F,Cl,Br R = C₂H₅</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-C’H(CH₃)-Q-C’H(CH₃)-R</td>
<td>Q = -O-CH₂-, -COO-</td>
<td>R = C₂H₅, COO-C₂H₅</td>
<td></td>
</tr>
<tr>
<td>-C’H(CH₃)-Q-R</td>
<td>Q = -COO-, -CH₂-COO-</td>
<td>R = CₘH₂ₘ₊₁ (m = 1-8)</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Examples of chiral substituents.

4.1 Restriction of molecular rotations

Molecular dipole moment $p_i$ rotates together with LC molecule as a whole around its long axis but this rotation is hindered because of various restrictions. It means that both molecular short (lateral) axis and molecular dipole moment are directed in preferred orientation for longer time. The uncompensated molecular dipole moment is an origin of the spontaneous polarization within the SmC* layer.

Degree of molecular alignment with respect to the director can be described by an (orientational) order parameter $S_k$, which has very low value for orientation of the short axis. Measurable values of the spontaneous polarization are expected for $S_k > 10^{-3}$. The larger $S_k$ the higher probability of lateral molecular axes to be directed in preferred direction and the larger contribution of $p_i$ to $P_s$.

Steric hindrances participate in a restriction of molecular rotations very effectively. In this respect the chiral centre, depicted as an uneven tripod with unequally long arms (see Fig. 2), plays an important role. With increasing asymmetry of the tripod its restrictive effect as well as $S_k$ increases. This effect has been observed for numerous compounds (Chin et al., 1988; Nakauchi et al., 1984; Sakurai et al., 1984; Yoshizawa et al., 1989), some examples of compounds with the chiral centre -C’H(CH₃)-CₘH₂ₘ₊₁ are shown in Table 2. Of course, the increase of $P_i$ in this way is limited. An optimal length of the aliphatic chain exists for which $P_i$ has a maximal value and additional lengthening leads to the spontaneous polarization decrease (see Table 2).

On the other hand branching of a terminal substituent and lengthening of aliphatic chains suppresses in many cases thermal stability of the mesophase narrowing the temperature

1 Orientational order parameter, $S_k$ characterizes degree of molecular alignment with respect to the director. It takes the values between zero and one. For a completely random and isotropic sample, $S=0$, whereas for a perfectly aligned sample $S=1$. 

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range of the mesophase or fully prevents its formation. This negative effect can be compensated by elongation of the central linear rigid core of the molecule. Therefore, the most of ferroelectric liquid crystals with strongly asymmetric chiral center \( R^* \) (\( m=6 \)) has three aromatic or heteroaromatic rings in the central core.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( m )</th>
<th>( P_s ) (nC cm(^{-2} ))</th>
<th>SmC* range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>2</td>
<td>130</td>
<td>68 - 130</td>
</tr>
<tr>
<td>II</td>
<td>6</td>
<td>403</td>
<td>60 - 132</td>
</tr>
<tr>
<td>II</td>
<td>8</td>
<td>210</td>
<td>70 - 125</td>
</tr>
<tr>
<td>III</td>
<td>1</td>
<td>26</td>
<td>103 - 120</td>
</tr>
<tr>
<td>III</td>
<td>3</td>
<td>70</td>
<td>52 - 110</td>
</tr>
<tr>
<td>III</td>
<td>5</td>
<td>29</td>
<td>49 - 96</td>
</tr>
</tbody>
</table>

Table 2. Temperature range of the SmC* mesophase and maximum values of the spontaneous polarization \( P_s \) for compounds II (Yoshizawa et al., 1989) and III (Nakauchi et al., 1989). Influence of the chiral centre asymmetry.

Combination of mentioned chiral centre with tricyclic rigid molecular core of the ester type provided first chemically stable substances

\[
C_nH_{2n+1}OOCOOC\bulletH(CH_3)\cdot CH_2\cdot COO\cdot C_mH_{2m+1}
\]

with rather high spontaneous polarization \( (P_s \approx 50 \text{ nC cm}^{-2}) \) (Inukai et al., 1986). First commercial ferroelectric mixtures (Japan CHISSO Corp.) designed for electro-optical applications working in a broad temperature range around room temperature were based on the mentioned compounds. Similarly, the first Czech experimental memory electro-optical cells with surface stabilized ferroelectric liquid crystal (SSFLC) were realized with this material already in the year 1987 (Pirkl, 1990).

It is hardly possible to assess unambiguously the effect of others factors on molecule rotation either for lack of data, or because of combination of impacts (e.g. a side substituent on the central core in addition to the steric constraint brings also a significant transverse dipole moment).

### 4.2 Restriction of intramolecular rotations

Strength of the spontaneous polarization can be increased considerably by restricting the freedom of the chiral center rotation in relation to the molecule as a whole. Many single bonds in FLC molecules enable more or less independent rotation of particular parts of the molecule around its long axis. This is regarded as the second main reason of a low contribution of molecules to resulting dipole moment of the smectic layer. The lowering is particularly strong if the dominant transversal molecular dipole moment rotates independently of the chiral group.
Generally, shortening the distance and lowering the amount of longitudinal bonds between the position of the molecular transverse dipole moment and asymmetric carbon is regarded as a way for suppressing the negative influence of intramolecular rotations. The most radical way would be to introduce the dipole moment directly to the chiral group, as will be discussed below.

Definitely, the methyl group located at the linkage position Z lowers the $P_s$ value significantly (see Table 3).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>$P_s$ (nC cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IV</td>
<td><img src="image1" alt="Structure IV" /></td>
<td>-18</td>
</tr>
<tr>
<td>V</td>
<td><img src="image2" alt="Structure V" /></td>
<td>3</td>
</tr>
</tbody>
</table>

Table 3. Maximum values of the spontaneous polarization $P_s$ for compounds IV (Sakurai et al., 1984) and V (Uemoto et al., 1981). Influence of a bridge group Z ($-\text{CH}_2-$).

The effect of various molecular constituents should not be considered separately, as the complex molecular configuration plays a role. For example, the characteristic free rotation of both rings about the central linkage of biphenyl group can be restricted by suitable neighboring groups, which increases the order of the chemical bond due to mesomeric effect. The result of this conception is documented in Table 4. In compound VI one can suppose that mesomeric as well as induction effect increase the dipole moment of the central carbonyl group and together with strongly asymmetric chiral centre bring about the increase of the $P_s$ value.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>$P_s$ (nC cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VI</td>
<td><img src="image3" alt="Structure VI" /></td>
<td>100</td>
</tr>
<tr>
<td>VII</td>
<td><img src="image4" alt="Structure VII" /></td>
<td>76</td>
</tr>
<tr>
<td>VIII</td>
<td><img src="image5" alt="Structure VIII" /></td>
<td>48</td>
</tr>
</tbody>
</table>

Table 4. Values of the spontaneous polarization $P_s$ at temperatures $T_c - 20 ^\circ C$ below the SmC*-SmA transition (Inukai et al., 1986). Influence of the mesomeric effect.

4.3 Enhancement of transversal molecular dipole moment

Enhancement of the transversal molecular dipole moment represents one of the effective ways for the increase of the $P_s$ value, the location of this dipole moment as well as the volume of the lateral substituent being important. In the absolute majority of FLC one of the functional group built in the central skeleton or in the linkage group Z is the source of the transversal dipole moment. Frequently it is the carbonyl group $>\text{C}=\text{O}$, the dipole moment of which can be increased due to mesomeric effect.
The additional increase of $P_s$ can be achieved by lateral substitution of electronegative atoms or functional groups that behave as acceptors of electrons. The location of the substitution is very important for the increase of $P_s$. In the following, two main cases are considered separately.

### 4.3.1 The effect of the lateral substitution on molecular core

This substitution is effective in the vicinity of the asymmetric carbon as well as on distant parts of the central skeleton. It brings additional transversal dipole moment and influences steric hindrance of both rotations of molecules about the longitudinal axis and intramolecular rotations. Besides, the lateral substituents may influence the temperature stability of the mesophase. Halogens (F, Cl, Br), nitril group (-C≡N), or methyl group (-CH$_3$) are the mostly used substituents. One of the possible effects of such substituents is shown in Table 5.

<table>
<thead>
<tr>
<th>X</th>
<th>$P_s$ (nC cm$^{-2}$)</th>
<th>SmC*$^*$ range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>76</td>
<td>78 - 103</td>
</tr>
<tr>
<td>F</td>
<td>85</td>
<td>52 - 104</td>
</tr>
<tr>
<td>Cl</td>
<td>161</td>
<td>31 - 78</td>
</tr>
<tr>
<td>Br</td>
<td>166</td>
<td>44 - 66</td>
</tr>
<tr>
<td>CN</td>
<td>189</td>
<td>41 - 57</td>
</tr>
</tbody>
</table>

Table 5. Values of the spontaneous polarization $P_s$ (nC cm$^{-2}$) at temperatures $T_c - 10$ °C and a temperature range of the SmC*$^*$ mesophase. Influence of a substitution on the central core near an asymmetric carbon in an ortho position to the linkage group Z (−O−), (Furukawa et al., 1988).

With increasing volume of the substituent thermal stability of the mesophase decreases and its temperature range becomes narrower. The substitution of chlorine appeared as the optimal one. The significant increase of $P_s$ is a result of two effects: in preferential conformation specified by MM method (Furukawa et al., 1988) the dipole moments of C-X bond and ether group –O- are nearly parallel and thus are added up (see Fig. 4a) and simultaneously the steric hindrance in the chiral centre between the phenyl and methyl group restricts the rotation of the chiral group.

For another type of the central skeleton the expected increase of $P_s$ occurs in the following sequence of substituents H $<$ F $<$ Cl $<$ Br $<$ CN (see Table 6). On the other hand the influence on the thermal stability of the mesophase is lower and not so unequivocal (Furukawa et al., 1988).

Fig. 4. Preferential conformation and mutual orientation of dipole moments $p_i$ and polar groups near the chiral centre of compounds IX (a) and XVII (b).
Table 6. Values of the $P_s$ at temperatures $T_c - 10\,^\circ C$ and a temperature range of the SmC$^*$ mesophase. Influence of a substitution on the central core near an asymmetric carbon in an ortho position to the linkage group Z (−O−), (Furukawa et al., 1988).

Probably the best result has been found for the substitution by the nitrogroup (−NO$_2$) as is shown for compound XIII in Table 7.

Table 7. Maximum measured values of the spontaneous polarization $P_s$ at compounds XII (Inukai et al., 1986), XIII and XIV (Walba et al., 1991). Influence of a substitution on the central core near the asymmetric carbon in an ortho position to the linkage group Z.

In Table 8 one can mention positive impact of the various lateral substitutions located on the molecular end opposite to the asymmetric carbon (Pachomov, 1997; Hamplová et al., 2007) on the increase of the spontaneous polarization $P_s$. The methoxy substitution was the only resulting in the decrease of $P_s$, which has not been reliably explained so far.

On the other hand increase of $P_s$ due to lateral substituent cannot be expected e.g. when connecting group Z is formed by carboxyl –COO-. Then at the preferential conformations the dipole moments of C-X and C=O bonds are antiparallel (see Fig. 2b) resulting in a decrease of $P_s$, which is shown in Table 9. Thus proximity of polar group and the chiral centre does not assure increase of $P_s$ (Furukawa et al., 1988).

The value of the spontaneous polarization can be also significantly increased when the phenyl ring in the central core is exchanged for the heterocycle (mainly nitrogenous). An example with pyrimidine core is given in Table 10.
Table 8. Values of the $P_s$ (nC cm$^{-2}$), at a substitution of the central core far from asymmetric carbon in the meta position to the non-chiral substituent R (Pachomov, 1997). Values of the $P_s$ at $T = T_c - 10^\circ$ C (unless otherwise indicated).

Table 9. Values of the $P_s$ at a substitution of the central core near the asymmetric carbon in the ortho position to the linkage group Z (Furukawa et al., 1988). Values of the $P_s$ at $T = T_c - 10^\circ$ C.

Table 10. Rise of the spontaneous polarization $P_s$ owing to a heterocyclic ring in the central core of molecule (Hirai et al. 1992). Values of the $P_s$ are maximal measured.

4.3.2 The effect of the lateral substitution on the asymmetric carbon
Introduction of the transversal dipole moment directly to the chiral centre proved to be efficient, as it eliminates intramolecular rotations. The impact of this type of substitution on $P_s$ values is shown in Table 11. The substitution of fluorine in various configurations
Increased the $P_s$ values up to the factor of 8. Introduction of chlorine gives still higher increase of $P_s$ (cf. compounds XXIV and XXV in Table 12). The value of $P_s$ has been still doubled in compound XXVI with additional asymmetric carbon introduced in the chiral group (Table 12).

Table 11. Influence of fluorine atom in the chiral centre on the spontaneous polarization $P_s$ at temperatures $T = T_c - 20^\circ$ C (Hirai et al., 1992).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$R$</th>
<th>$P_s$ (nC cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XX</td>
<td>$\text{H} (\text{CH}_3)-\text{C}_4\text{H}_9$</td>
<td>15</td>
</tr>
<tr>
<td>XXI</td>
<td>$\text{H} (\text{CF}_3)-\text{C}_4\text{H}_9$</td>
<td>98</td>
</tr>
<tr>
<td>XXII</td>
<td>$\text{H} (\text{F})-\text{C}_4\text{H}_9$</td>
<td>86</td>
</tr>
<tr>
<td>XXIII</td>
<td>$\text{F} (\text{CH}_3)-\text{C}_4\text{H}_9$</td>
<td>122</td>
</tr>
</tbody>
</table>

Table 12. Maximal values of the spontaneous polarization $P_s$ at compounds XXIV (Terashima et al., 1986), XXV and XXVI (Bahr & Heppke, 1986).

The FLCs consisting of molecules with the heterocycle in the molecular core usually have rather high values of the $P_s$. Therefore, combination of the fluorine substitution with heterocyclic compounds yields very good results for the $P_s$ values as it is demonstrated in Table 13.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$R$</th>
<th>$P_s$ (nC cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XXIV</td>
<td>$(\text{CH}_3)\text{-C}_2\text{H}_5$</td>
<td>6</td>
</tr>
<tr>
<td>XXV</td>
<td>$(\text{Cl})\text{-CH(\text{CH}_3)}_2$</td>
<td>140</td>
</tr>
<tr>
<td>XXVI</td>
<td>$(\text{Cl})\text{-C}^*\text{H(\text{CH}_3)}\text{-C}_2\text{H}_5$</td>
<td>290</td>
</tr>
</tbody>
</table>

Table 13. Combined influence of the fluorine substitution in the chiral centre with the heterocycle in the molecular core on the spontaneous polarization $P_s$ at temperatures $T = T_c - 10^\circ$ C (Hirai et al., 1992).
From Tables 11 and 13 one can infer the role of the exact position of the halogen substitution on the asymmetric carbon. It is seen that the substitution of the hydrogen atom results in the highest $P_s$ value.

In contrast to the substitution on the molecular core the effect of the halogen on $P_s$ increases according to sequence $\text{Br} < \text{Cl} < \text{F}$ (see Table 14). As the differences in the dipole moment of the C-X bond are small, apparently the volume of the halogen atom plays a role. Extremely high $P_s$ has been found for compounds based on 5-alkylpentano-5-lactone (Nakauchi et al., 1989; Sakashita et al., 1992). Such high values results from a synergic effect of two asymmetric carbons (see Table 15) and a polar group located directly in the chiral centre, which represents steric precondition for hindering of the molecular rotation.

Table 14. Values of the spontaneous polarization $P_s$ at temperature $T = T_c - 10^\circ$ C. Influence a substitution with halogen atom on asymmetric carbon (Sierra et al., 1992).

Table 15. Maximum measured values of the spontaneous polarization $P_s$ at compounds with a valerolactone chiral centre at temperature $T = T_c - 10^\circ$ C, XXXI (Nakauchi et al., 1989) and XXXII (Sakashita et al., 1992).

4.4 Other effects

Properly chosen linkage Z can be significant for increase of the $P_s$ value, as it is evident from Table 16.

Table 16. Influence of the linkage group Z on the spontaneous polarization $P_s$.

Another factor, which favorably affects the spontaneous polarization, is presence of more polar groups with a suitable preferential conformation near the asymmetric carbon atom. For example see substances with the lactic acid moiety in which the chiral carbon atom is
flanked by two lateral dipoles $p_i$ (Fig. 5). Because of the proximity of the methyl group on the central chiral atom to adjacent lateral carbonyl dipoles and consequent steric hindrance, such arrangement may produce materials with relatively high $P_s$ (see Table 17).

![Fig. 5. A chiral centre with the asymmetric carbon atom which is flanked by two lateral carbonyl dipoles (R is non-chiral aliphatic chain)](image)

Table 17. Temperature range of the SmC* mesophase, maximum measured values of the spontaneous polarization $P_s$ (nC cm$^{-2}$) and values of the $P_s$ at temperatures $T = T_c - 20^\circ$C at compounds XXXIII (Zu-Sheng Xu et al., 1999) and XXXIV (Kašpar et al., 2004).

<table>
<thead>
<tr>
<th>Compound</th>
<th>SmC* range ($^\circ$C)</th>
<th>$P_s$ ($T_c-20^\circ$C)</th>
<th>$P_s$ (max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XXXIII</td>
<td>96 - 145</td>
<td>120</td>
<td>210</td>
</tr>
<tr>
<td>XXXIV</td>
<td>79 - 101</td>
<td>117</td>
<td>117</td>
</tr>
</tbody>
</table>

The FLCs consisting of molecules with two or more asymmetric carbon atoms at one end usually have rather high $P_s$. Nevertheless, there is not a simple relation between the value of $P_s$ and a number of $C^*$ atoms. The chiral centre configuration namely relative orientation of dipole moments around the asymmetric carbon atoms, and degree of intramolecular rotation hindrance play an important role. The situation can be illustrated on a rather rare compound with three asymmetric carbon atoms (XXVII, Table 18). In this compound, CH$_2$ linkage between the second and third asymmetric carbon atoms has non-convenient influence on $P_s$.

Table 18. Temperature range $\Delta T$ of the SmC* mesophase and maximum measured values of the spontaneous polarization $P_s$. Influence of number of the asymmetric carbon atoms at compounds XXXV (Taniguchi et al., 1988) and XXXVI, XXXVII (Kašpar et al., 2001).

<table>
<thead>
<tr>
<th>Compound</th>
<th>R</th>
<th>$\Delta T_{\text{SmC}^*}(^\circC)$</th>
<th>$P_s$ (max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XXXV</td>
<td>$C^*(\text{H}_3)\text{-COO-C}_6\text{H}_5$</td>
<td>3 - 61</td>
<td>55 nC cm$^{-2}$</td>
</tr>
<tr>
<td>XXXVI</td>
<td>$C^<em>(\text{H}_3)\text{-COO-}C^</em>(\text{H}_3)\text{-COO-C}<em>6\text{H}</em>{13}$</td>
<td>59 - 88</td>
<td>93 nC cm$^{-2}$</td>
</tr>
<tr>
<td>XXXVII</td>
<td>$C^<em>(\text{H}_3)\text{-COO-C}^</em>\text{(H}_3)\text{-COO-CH}_2\text{-C}^*(\text{H}_3)\text{-C}_6\text{H}_5$</td>
<td>98-104</td>
<td>113 nC cm$^{-2}$</td>
</tr>
</tbody>
</table>
Very high spontaneous polarization was established for compounds with strongly fluorinated terminal alkyl chains (Table 19). Such compounds exhibit also antiferroelectric phases (SmC\textsubscript{A}\*). Other effects, e.g. number of carbon atoms in the linear aliphatic chain far-away from the chiral centre, are less important and often also ambiguous.

<table>
<thead>
<tr>
<th>XXXVIII</th>
<th>(P_s = 155 \text{ nC cm}^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_3\text{CH}_2\text{CH}_2\text{COO}-(\text{CH}_2)_5\text{O}\text{COO}-(\text{CH}_2)_5\text{O}\text{COO}-\text{C}'\text{H}(\text{CH}_3)\text{C}<em>6\text{H}</em>{13})</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>XXXIX</th>
<th>(P_s = 340 \text{ nC cm}^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CF}_3\text{CF}_2\text{CF}_2\text{COO}-(\text{CH}_2)_3\text{O}\text{COO}-(\text{CH}_2)_3\text{O}\text{COO}-\text{C}'\text{H}(\text{CH}_3)\text{C}<em>6\text{H}</em>{13})</td>
<td></td>
</tr>
</tbody>
</table>

Table 19. Values of the spontaneous polarization \(P_s\) at temperatures \(T = T_c - 30^\circ\text{C}\). Influence of fluorination of the terminal alkyl chain R (Dabrowski, 2000).

5. Ferroelectric liquid crystalline materials for applications

The value of the spontaneous polarization \(P_s\) is a crucial parameter for behavior of FLCs in an electric field and thus must be carefully optimized for specific electro-optical cells. Other parameters as the helical pitch length, optical and dielectric anisotropy, viscosity and tilt angle value are important as well for satisfying operation of different FLC electro-optic equipments (e.g. displays). Furthermore, the type of the mesophase existing at temperatures above the FE SmC\* phase (either the cholesteric or the smectic A\* phase) is important for alignment of the liquid crystalline materials in the electro-optic cells. Unfortunately, it is quite impossible to find all suitable properties for practical use in one ferroelectric compound. The only solution how to create a suitable material with desirable properties is mixing of several liquid crystalline components, both chiral and non-chiral substances.

Typically, an eutectic non-chiral SmC mixture is prepared with desirable properties that are stable in a wide temperature range (including room temperature). Ferroelectricity is then induced by adding a suitable chiral dopant exhibiting the SmC\* phase. For this purpose the spontaneous polarization of this dopant must be extremely high in order to achieve a desirable \(P_s\) value of the mixture with the lowest concentration and thus with only a minimum affection of others parameters. The use of only low amount of chiral dopant in the resulting FE material intended for application also lower the costs, as the chiral component is by far its the most expensive ingredient.

Single compounds with extremely high \(P_s\) (or possibly mixtures of them) are applied only for realization of fast modulated electro-optical cells (10\textsuperscript{6} Hz) on the basis of electroclinic effect in the SmA\* mesophase.

6. Banana liquid crystals

In 1996 new polar phases have been discovered in materials composed of molecules with a bent-core (Niori et al., 1996). Such molecules are bent-shaped (banana) and can create, so called banana liquid crystals. As an example two formulas of the molecules creating banana liquid crystals are shown for example in Table 20.
Table 20. Examples of the bent-core (banana) molecules XL (Matsunaga & Miyamoto (1993) and XLI (Kašpar et al. (2002)).

Molecular models of a typical rod-like molecule (VIII) and banana-like molecule (XL) are presented for comparison in Figure 6.

Fig. 6. Three dimensional molecular models of a rod-like molecule (VIII) with the asymmetric atom (pink colored) and banana-like molecule (XL).

Packing of these molecules in the smectic layers creates the structural layer chirality even though the molecules are non-chiral. Moreover, the mesomorphic properties of the bent-shaped compounds are richer than those of classical materials with rod-like molecules. So far 8 types of so-called B-phases have been discovered and their structural properties investigated. These new mesophases are denoted by the letter B, which refers to the characteristic bent or banana molecular shape. Chronologically the terms B1, B2, B3, etc have been used in the literature to designate different phases as they were discovered (for review see e.g. Pelzl et al. 1999; Takezoe & Takanishi, 2006; Reddy et al. 2006). Among them, only B2 phase (sometimes denoted as SmCP) is fully and easily switchable. This phase exhibits mostly AF and quite exceptionally FE properties. The first FE banana B2 phase was reported in (Gorecka et al. 2000) for a compound with bent-shaped molecules, but with a chiral centers introduced in end chains. In non-chiral bananas the FE phase has been found mostly for non-symmetrical bent-shaped molecules (Novotná et al. 2006) or for molecules having a hockey-stick form (see Fig. 7).
It was found that B2 phase exhibits typically strong non-linear electro-optic effect and subsequently strong SHG signal exceeding by several orders the SHG signal of classical liquid crystals (Novotná et al, 2008). The spontaneous polarization is typically up to the order of several hundreds, usually more than 700 nC cm\(^{-2}\) (Pelzel et al., 1999; Reddy et al., 2006). These properties indicate potential of these materials in pyro- or piezo-electric applications. Of course, despite extensive work in this area, many questions remain to be answered. Among others, sample alignment is not only goal for applications but also for basic research.

Liquid crystals composed of molecules having hockey-stick form (see Fig. 7) represent an intermediate material in which phases typical for both rod-like and bent-shaped molecules can exist in different temperature ranges or in different homologues. Thus they exhibit nematic phases as well as smectic FE and AF phases, in some cases also banana type phases as B2 (Reddy et al., 2006; Novotná et al., 2008). Investigation of various forms of molecules that can form liquid crystalline state can help to explain some general structure-property relationships concerning the formation of polar order and structural chirality.

In any case, the investigation of bent shaped liquid crystals is a typical multidisciplinary field where many questions remain still open.

7. Conclusions

Hundreds of thousands of FE liquid crystals have been synthesized and characterized so far. Still full data on the spontaneous polarization are not available for overwhelming part of them, particularly in case the \(P_s\) is temperature dependent. This is one of the reasons why it is difficult to find definite molecular configuration for a compound with value of \(P_s\) desired for a specific application. The other reason is strongly complex influence of each molecular structural feature on the resulting material properties. This contribution formulates main general rules that lead to increase of \(P_s\), namely increase of lateral molecular dipole moment and hindering of both molecular and intramolecular rotations. It is also shown that the problem solving is not straightforward as each step may cause non-intended negative effects on the stabilization of the FE phase in sufficiently broad and low temperature range, which is demanded for technical applications. Also the nature of the high temperature phase (above the FE one), which is also watched when considering specific applications, can be easily influenced by even slight change of the molecular structure. In summary, the results discussed here can be useful for designing the molecular structure for applications. Besides, they contribute to general knowledge on the molecular structure – material property relation in liquid crystals. Some important problems yet remain to be solved. Nevertheless, ferroelectric liquid crystals gain a niche market, for example, in fast
high-resolution microdisplays for near-eye applications, such as view-finders for digital cameras or camcorders.

8. Acknowledgment

This work was financially supported by the Ministry of Education, Youth and Sports of Czech Republic under the research project VZ1 MSM0021627501 and the Czech Science Foundation project No. 204/11/0723.

9. References


Bone, M.F.; Bradshaw, M. J.; Chan, L. K. M.; Coates, D.; Constant, J.; Gemmell, P. A.; Gray, G. W.; Lacey D.


Ferroelectric Liquid Crystals with High Spontaneous Polarization


Ferroelectric materials have been and still are widely used in many applications, that have moved from sonar towards breakthrough technologies such as memories or optical devices. This book is a part of a four volume collection (covering material aspects, physical effects, characterization and modeling, and applications) and focuses on the underlying mechanisms of ferroelectric materials, including general ferroelectric effect, piezoelectricity, optical properties, and multiferroic and magnetoelectric devices. The aim of this book is to provide an up-to-date review of recent scientific findings and recent advances in the field of ferroelectric systems, allowing a deep understanding of the physical aspect of ferroelectricity.

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