Polar Bent-Shape Liquid Crystals - From Molecular Bend to Layer Splay and Chirality

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Considerable progress has been achieved in understanding the fascinating structure and physical properties of the ferroelectric liquid crystalline phases formed by bent-core liquid crystals (BLC). In this review, we discuss a manifold of polar structures and phases found in BLCs such as orthogonal and tilted ferro-/antiferroelectric phases, smectic phases, switchable columnar phases, modulated structures and phases stabilised by a periodic lattice of defects such as dark conglomerate and nanofilament phases. We review the theoretical aspects of ferroelectricity in BLCs including existing microscopic theories and computer simulations, polarity and chirality phenomena. The last part of the paper is devoted to the peculiarities of the behavior of BLCs in a restricted geometry (freely suspended films and filament) and the perspective technological applications.

1 Introduction

The first liquid crystals of bent core (bent-shaped or banana-shaped) molecules were synthesized and reported by Vorländer in 1929 (ref. 1 and 2) without any impact for over 60 years. The rebirth in interest for bent-core mesogens can be attributed to theoretical and technological interest towards ferroelectric liquid crystalline phases that, until the 1990’s, were only observed in tilted smectic phases of chiral calamitic and discotic molecules.3–6 There the simultaneous presence of the molecular chirality and director tilt lead to a polar order (tilt + chirality = polarity), because chirality breaks inversion symmetry, a condition needed for polar order.7 However synthesis of chiral materials is expensive; therefore a great deal of theoretical and experimental efforts was put into finding ferroelectric liquid crystals using achiral molecules.8–21 These efforts yielded to a variety of interesting methods and materials including polyphilics that were hoped to form ferroelectric phase by polar nano-segregation of their different units;13 or some main-chain liquid crystal polymers having different aliphatic spacers with odd numbers of carbons incorporated into the backbone in a regularly alternating fashion where they segregate into different microdomains.14 In part of these studies Tredgold10 realized that a molecule with a bow shape would have a spontaneous polarization, and therefore would be ferroelectric. In 1991 Matsunaga and coworkers15,16,22 synthesized achiral bent-core materials, and found that they could form smectic liquid crystals, where the ferroelectricity is
ascribed to the polar $C_{2v}$ symmetry obtained from the efficient packing of bent-core (banana-shaped) molecules into layers. Simultaneously with the synthesis of bent-core molecules, Brand, Cladis and Pleiner\textsuperscript{12,24} discussed the symmetry of the smectic phases consisting of several types of molecules, including board and bent-core, and pointed out the possible emergence of polar smectic phases. For the same symmetry reason polymer–monomer mixtures were also found\textsuperscript{25} to show antiferroelectric polarization in bilayered smectic C, while the two components of the mixtures alone showed no antiferroelectricity. Columnar phases of pyramidal shaped molecules have been observed to be ferroelectric as well\textsuperscript{26,27} and other novel complex shaped molecules appeared to emerge as contenders in the race for fast switching and versatile ferroelectric devices.

When bent-core molecules pack in a condensed liquid crystal phase they tend to fill the space as effectively as possible. For this reason, without any steric substituents, or electrostatic “bumps” in their structures, they tend to form layers, i.e., smectic phases. The tendency for layering combined with the close packing requirement, results in a polar order along the direction of molecular bows. This results in monodomains with a finite residual (spontaneous) macroscopic electric polarization $P$ (volume density of the molecular dipoles). It is a direct result of sterically induced alignment of the molecular bows of achiral mesogens. In the case of cylinders, polar order is possible only when they are chiral and tilted. For instance, in SmC\textsuperscript{*} materials the molecular chirality and director tilt together result in polar order,\textsuperscript{2} i.e., the primary order parameter is the tilt angle $\theta$, which governs $\vec{P}$ (improper ferroelectricity). When the polarization can be switched by electric field, we talk about ferroelectricity. Experimentally, $\vec{P}$ is usually determined in electrooptical switching experiments: under applied periodic rectangular or triangular waveforms, the switching of the spontaneous polarization $\vec{P}$ induces a transient electric current peak in each half period of the driving field.\textsuperscript{29} As the spontaneous polarization of single smectic layers increases, the ferroelectric structure becomes unstable. Such materials with large layer polarizations ($P > 10^{-3}$ C m\textsuperscript{-2}) form antiferroelectric phases with the layer dipole moments aligned antiparallel in adjacent layers. Antiferroelectric liquid crystals show double current peaks in each half period of triangular waveforms.

In this review we summarize the main findings of polar bent-shaped smectic and columnar liquid crystals. The review is organized as follows. In Section 2 we discuss the theoretical aspects including the main macroscopic theories, polarity-chirality issues, phase structures and computer simulations. Section 3 describes the main experimental results of simple smectics, such as the SmAP, SmCP and SmC\textsubscript{b} phases. Section 4 deals with the modulated smectics including SmCP\textsubscript{mod} and SmAP\textsubscript{mod}, the dark conglomerates and nanoﬁlaments. Section 5 is devoted to the ferroelectric columnar phases, Section 6 summarizes other polar systems, such as free-standing polar films and ﬁlaments, ferroelectric crystals, and the possible role of ferroelectricity in nematics. Finally Section 7 lists several possible applications of bent-core ferroelectrics.

2 Theoretical considerations

2.A Theories

Exhaustive symmetry based classification of bent-core smectic phases has been given by Brand et al.\textsuperscript{24,29} Various types of biaxial smectic phases have been suggested by the authors and labeled with various $C$ symbols listed in Table 1, although some of these phases are of orthogonal, i.e., SmA-type. One of the most important outcomes of this theory is that biaxiality of the molecular shape and polar order can give rise to a manifold of smectic phases with a fluid order including chiral, ferro-, anti-ferro- and helielectric phases (Table 1).

Using Landau theory, a variety of tilted polar smectic phases originating from polar order have been shown by Roy et al.\textsuperscript{28} The free-energy expression suggested by the authors reflects the achiral structure of the bent-core mesogens and contains no linear coupling terms specific for the chiral SmC\textsuperscript{*} phase:

\[
F_{h} = \frac{a}{2} \xi^{2} + \frac{b}{24} \xi^{4} + \frac{\alpha}{2} P^{2} + \frac{\beta}{4} P^{4} + \delta_{1} \xi^{2} P^{2} + c \left( \vec{z} \cdot \vec{P} \right)^{2} + \frac{1}{2 \chi_{0}} \left( \vec{n} \cdot \vec{P} \right)^{2} + \frac{1}{2 \chi_{1}} \left( \vec{k} \cdot \vec{P} \right)^{2} + d_{1} \xi^{2} \left( \vec{n} \cdot \vec{P} \right)^{2} + d_{2} \xi^{2} \left( \vec{k} \cdot \vec{P} \right)^{2} + d_{3} \left( \vec{n} \cdot \vec{P} \right) \left( \vec{k} \cdot \vec{P} \right) - \vec{E} \cdot \vec{P} \tag{1}
\]

where $a$, $b$, $\alpha$, $\beta$ are phenomenological coefficients of the Landau expansion, $\vec{P}$ is polarization, $\xi$ is the tilt (axial vector), $\vec{n}$ is the director, $\vec{k}$ is the normal to the smectic layers, and $\vec{E}$ is the external electric field. This model yields five different phases in a field-free state: (1) a monoclinic phase with $C_{h}$ symmetry and polarization in the tilt plane of the mesogens, (2) a transversely polarized phase of monoclinic $C_{2}$ symmetry with $\vec{P}$ perpendicular to the tilt plane, (3) a transversely polarized SmA-type phase with the $C_{2v}$ symmetry, and (4) a dielectric SmC\textsubscript{h} phase without spontaneous polarization, and (by adding an eighth-order polarization-tilt coupling term) a double-tilted SmC\textsubscript{a} phase with triclinic $C_{1}$ symmetry. This model shows that the existence of a $\vec{P}$ does not require a director tilt, i.e., polar bent-core phase are proper ferroelectrics. Although no chiral terms are allowed in eqn (1), phases with chiral symmetries also occur in this model as a result of a spontaneous breaking of achiral symmetry.

Another theoretical approach to understand the development of bent-core phases was suggested by Lorman and Metcalf.\textsuperscript{21} The attention of the authors was drawn by the fact that the majority of bent-core compounds show tilted and polar phases.

<table>
<thead>
<tr>
<th>Phase</th>
<th>SmA</th>
<th>SmP</th>
<th>SmQ</th>
<th>SmC</th>
<th>SmCp</th>
<th>SmCQ</th>
<th>SmCr</th>
<th>SmC2</th>
<th>SmC2v</th>
<th>SmC1h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Symmetry</td>
<td>$D_{2h}$</td>
<td>$C_{2v}$</td>
<td>$C_{1h}$</td>
<td>$C_{1}$</td>
<td>$C_{2}$</td>
<td>$C_{2h}$</td>
<td>$C_{1h}$</td>
<td>$C_{1}$</td>
<td>$C_{1}$</td>
<td>$C_{2}$</td>
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symmetry group tentatively attributed to the so-called B7 structures that show applicability to columnar and so helical superstructures.

polarized waves and describes the SmAP A phase with diagram:

types of phases can be encountered in the minimal phase wave of polarization, and a wave of tilt. In this model, three types of phases can be encountered in the minimal phase diagram:

- A rectilinear R-phase, which has a structure of linearly polarized waves and describes the SmAP_h phase with D_{2h} symmetry.
- An EL phase with elliptic polarization belonging to the symmetry group D_{2}, which is a chiral antiferroelectric structure and corresponds to chiral SmCP phases.
- A C-phase, where the wave vectors are circularly polarized, tentatively attributed to the so-called B7 structures that show helical superstructures.

Further development of the wave-vector model showed its applicability to columnar and soft-crystal phases. Considering the condensation of several nonparallel wave vectors, up to 24 different phases can be obtained in the frame of this model, including orthorhombic, monoclinic and triclinic structures describing nearly all known phases formed by bent-core mesogens.

A microscopic model of the bent-core phases has been developed by Emelyanenko and Osipov. The interaction energy was approximated by the electrostatic and dispersion forces acting between molecules modeled by pairs of spherocylinders. It was shown that in a perfectly ordered smectic phase the distributed dispersion interaction between bent-core molecules stabilizes the spontaneous polarization and may be responsible for the tilt of the director. The orientation of the spontaneous polarization is determined by the balance between the dispersion and electrostatic dipole–dipole intermolecular interactions. The case when the spontaneous polarization is directed perpendicular to the tilt-plane corresponds to the SmCP phase.

The nematic phase of bent-shape molecules is much less common, and exists only in those molecules which have some large steric or electrostatic inclusions in their core, such as CN–, CH3, Cl, that disrupts their locking into a smectic phase directly below the isotropic phase. The first complete theoretical description of possible nematic-like (without translational symmetry) phases was given by Lubensky and Radzihovsky. Considering the expansion of the mass-moment tensor of bent-core mesogens (modeled by three spheres), the authors showed that, in addition to a second-rank tensor order parameter Q^{ij}, a vector ρ^i, and third-rank tensor T^{ijk} order parameters are necessary. The resulting phase diagram is very rich and contains uniaxial, biaxial, polar nematics and phases with tetrahedral symmetry.

**Fig. 1** Four possible polar smectic structures formed by bent-shape molecules. Vectors indicate the layer polarization. In the SmAP phase, the average long molecular axis (along the line connecting the end points of a molecule) is normal to the smectic layers. In the SmCP structure, the long axis and the molecular plane tilt ("clinic") with respect to the layer normal (crossbars at the top of the molecules indicate a tilt away from the observer). The SmC_G (SmCTP) phase has a double tilted structure (G stands for general), i.e., the molecular plane and the long axis are tilted in different directions (T stands for the tilt along the molecular plane). The fourth possibility (SmTP) is where the long axis is tilted but the molecular plane remains parallel to the layer normal.

2.B Structural cartoons

The structures of the four polar fluid smectic phases predicted by the theoretical models above are illustrated in Fig. 1. The average orientation of bent-core molecules is given by three orthogonal unit vectors, ⃗n, ⃗m, and ⃗P; ⃗n is the unit vector along the long axis, ⃗m is normal to the molecular plane, and ⃗P is along the kink direction. The unit vector ⃗k characterizes the direction of the layers.

**Fig. 2** Schematic illustration of the ferroelectric SmAP_f and antiferroelectric SmAP_a phases.
The SmAP structure, where \( \hat{n} \) is parallel to the smectic layer normal \( \hat{k} \), is similar to the SmA phase of calamitic liquid crystals, except that now the layers are polar (that is why the letter “P” is added to the name) due to the close packing of the bent molecules. Even in this simplest case, however, one can have two distinct situations; the layer polarization \( \vec{P} \) in the subsequent layers can be either parallel or antiparallel, corresponding to ferroelectric (SmAPf) or antiferroelectric (SmAPa) subphases (see Fig. 2).

The phase where the molecular planes are tilted with respect to the layer normal, i.e., when \( \hat{m} \) is not perpendicular to \( \hat{k} \), is denoted by SmCP with “C” standing for “clinic”. Depending on whether the tilt directions are the same, or they are alternating in the subsequent layers, we distinguish between “synclinic” and “anticlinic” situations, and label them by the subscripts “s” and “a”, respectively. In the polar plane determined by \( \vec{P} \) and \( \hat{k} \), this tilt is illustrated by a cross-bar at the end of the molecules that is away from the observer. Combining these different situations with the ferroelectric and antiferroelectric polar packing possibilities, we have 4 different sub-phases: SmCpF, SmCaPF, SmCaPA, and SmCsPF. Such a notation with some variations was introduced by Link et al., and is widely used in the literature. Note that the SmCP layers have only a two-fold symmetry, i.e. they have the same symmetry as the chiral SmC\( ^* \) materials.

In principle, we can also envision that \( \hat{n} \) is tilted with respect to \( \hat{k} \), so that \( \hat{m} \perp \hat{k} \). This additional tilt is usually referred to as “leaning” and the phase might be called SmLP. However, the SmL phase is already known in liquid crystals\(^\text{37}\) (a hexatic tilted smectic phase), so we shall use the first letter “T” of “tipping” (which is the synonym for leaning), and name this phase as SmTP.

Although in all situations the individual layer polarizations may not be parallel to the smectic layers, the out-of-layer components average out for the SmTaPF and SmTsPA structures and their macroscopic symmetry would be the same as of the SmAP and SmCP phases (Fig. 3).

One can also imagine that both “clinic” and “tipping” happen simultaneously.\(^\text{36}\) We label those “double-tilted” structures with SmC\( ^\text{TP} \), where both tilts can independently be parallel or antiparallel in subsequent layers. Taking into account that the layer polarizations can either be parallel or antiparallel to each other, i.e., the phase is ferroelectric or antiferroelectric, we can have altogether eight different subphases, as illustrated in Fig. 4.

Although in all situations the individual layer polarizations may not be parallel to the smectic layers, the out-of-plane components average out for the SmC\( ^\text{T} \)\( _{PF} \) and SmC\( ^\text{T} \)\( _{PA} \) structures and their macroscopic symmetry would be the same as that of the SmAP and SmCP phases. The SmC\( ^\text{TP} \) structures can be equivalently described by a tilt of the molecular plane \( \hat{m} \), and a rotation of the layer polarization \( \vec{P} \) about the long axis \( \hat{n} \) by an angle \( \alpha \). Particularly, if \( \alpha = 0 \) or \( \pi \), we have the SmCP case; whereas \( \alpha = \pi/2 \) or \( 3\pi/2 \) correspond to the SmTP phase. All other angles mean the double tilted SmC\( ^\text{TP} \) phase. Double-tilted layers have triclinic symmetry (\( C_1 \) in Schönflies notation),

![Fig. 3](#) Possible single tilted bent-core smectic structures. Top row: illustration of the fluid in-plane order of the layer polarization, and 3 dimensional explanation of tilt. Middle row: 2-dimensional illustration of the 4 possible situations when only the molecular plane is tilted with respect to the layer normal; bottom row: 2-dimensional illustration of the 4 possible situations when only the long axis is tilted (leaned) with respect to the layer normal.
i.e., they are symmetric only with respect to a 360° rotation around the polar axis. Such a structure was theoretically predicted by de Gennes\(^{38}\) and was labeled as SmC\(_G\) (“G” stands for generalized) without specifying bent-core molecules.

### 2.C Structural chirality

In contrast to SmC* materials, in bent-core smectics the combination of polar packing and the tilt of the molecular planes makes the smectic layers chiral, even when the individual molecules are achiral. This is called layer chirality\(^{39}\) and is illustrated in Fig. 5.

The chiral order parameter can be described by a pseudoscalar quantity \(\chi\):\(^{39}\)

\[
\chi = 2(\vec{k} \times \vec{n})\cdot(\vec{k} \times \vec{n}) = \sin(2\theta) \times \cos \alpha
\]  

(2)

One can see that \(\chi = 0\) for the non-tilted SmAP (\(\sin 2\theta = 0\)) and for the leaning phase (\(\cos \alpha = 0\)), and the chirality is maximum in the SmCP phase (\(\cos \alpha = 1\)). This definition of the layer chirality takes into account the \(\vec{k} \to -\vec{k}\), and \(\vec{n} \to -\vec{n}\) symmetry of the material, and its maximum is 1 for an SmCP phase with \(\theta = 45°\).

If the smectic phase is ferroelectric\(^{40-42}\) and synclinic (SmC\(_{a}P\_A\)) or if it is antiferroelectric\(^{44}\) and anticlinic (SmC\(_{a}P\_A\)), then the material has a homogeneously chiral structure, with the same sign of \(\chi\) in consecutive layers. If the smectic phase is ferroelectric and anticlinic (SmC\(_{a}P\_F\)), or if it is antiferroelectric and synclinic (SmC\(_{a}P\_A\)), then the material has alternating right- and left-handed chiral layers, with alternating positive and negative values of \(\chi\). This latter possibility is generally called a “racemic” structure, although we might use an alternative term “antichiral”\(^{44}\) to emphasize the rigid alternation from layer to layer.

Chirality over the optical wavelength range is usually seen in the form of rotation of the polarization plane of a linearly polarized light crossing a chiral material (optical activity). In isotropic liquids optical activity requires chiral molecules, resulting typically in about 1 degree rotation of a light crossing a 1 cm slab. In liquid crystals molecular chirality usually leads to a helical structure, which enhances the optical activity so that the optical rotation can be as large as 100 deg \(\mu\text{m}^{-1}\) in some short pitch cholesteric or SmC* materials.
2.D Computer simulations

The development of polar order was also observed in several computer simulations. The mesogens were modeled by sets of soft beads and by pairs of hard sphero-cylinders (Fig. 6). The important parameters in those simulations were the opening angle (varied between 120° and 180°) and the length-to-diameter ratio (between 2 and 10). It was shown that steric interactions alone are capable of stabilizing both ferroelectric and antiferroelectric polar orders of smectic layers.

Lansac et al. considered excluded volume interactions between V-shaped sphero-cylinders by Monte Carlo simulations. Although no tilted phases occurred in this model, a transition between a non-polar SmA and an antipolar SmAP phase was found when the opening angle was as large as 167°. Remarkably, this angle is much larger than the opening angle of mesogens experimentally observed in common bent-core compounds (110°–145°). Monte Carlo simulations also illustrated achiral symmetry breaking in the nematic phase made of mesogens with large opening angles, producing helical arrangements of arbitrary sense. Molecular simulations, based on sphero-cylinders, could not capture the tendency to form tilted polar phases like the SmCP phase. To stabilize the molecular tilt additional intermolecular interactions, such as bumpiness imposed by the aromatic units, are required.

3 Simple smectics

Experimental observations of simple polar smectic phases of bent-core liquid crystals described in Section 2B were pioneered at the end of 1990’s and lead to the “banana mania” of the last decade. This intense research has been recently reviewed in several papers. Among the myriads of interesting experimental findings, here we concentrate only on the polarity, chirality issues and electric field induced transitions.

3.A Orthogonal smectic phases

Strong steric interactions of bent-core mesogens result in ferro- and antiferroelectric orthogonal phases. The first example of the orthogonal antiferroelectric SmAP2 phase was found by the Halle group using X-ray and electrooptical techniques. A distinguishing feature of this phase is the sporadic occurrence of the half-integer topological defects in Schlieren textures of planarly aligned samples. Although the polar order develops independently from the tilt in BLC, the two order parameters remain strongly coupled. A detailed theoretical model describing the behavior of the SmAP phases was suggested by Gorecka et al. and experimentally examined in resorcinol-derived compounds showing SmA-SmAP-SmCP mesomorphisms.

The ferroelectric SmAPs phase corresponds to the structure proposed originally by Niori et al., but observed only recently, probably because orthogonal SmAP structures are rare due to the strong tendency of the bent-core mesogens to tilt. Also, the ferroelectric state is preferred only when the neighboring layers are decoupled by means of modified terminal groups (such as siloxane) of the mesogens.

In addition to these biaxial antiferroelectric and ferroelectric orthogonal phases, Pociecha et al. reported a non-tilted, optically uniaxial Smectic-A phase, fully miscible with the SmA phase of rodlike mesogens. This phase is manifested by the remarkable dielectric susceptibility as high as 140, and is attributed to the long-living polar fluctuations with low inter-molecular coupling. Such materials are also characterized by a ferroelectric-type current response with induced polarization comparable with that of SmC* materials. They also exhibit a strong field-induced Second Harmonic Generation (SHG), but because they do not have a spontaneous polarization, they should be designated as superparaelectrics. In an XY-type model the superparaelectric behavior was attributed to a structure composed by randomly oriented ferroelectric (polar) layers with polarization $p_i$ in each successive layer. This structure is designated as an SmAPR phase. The full phase diagram is obtained by studying the coupling between the successive layers given by the expression for the Gibbs energy:

$$G = \sum_j \left( \frac{1}{2} a_{ij} (p_j \cdot p_{j+1}) + \frac{1}{4} b_{ij} (p_j \cdot p_{j+1})^2 \right)$$

where $a_{ij}$ and $b_{ij}$ are coupling constants. The phase diagram of this model shows both SmAPF and SmAPA phases, as well as a helical SmAPs, a bilayer SmAP2 and a SmAPR phase with a random direction of the polarization in the neighboring layers (Fig. 7).

Typical molecules forming orthogonal superparaelectric smectic phases are shown in Fig. 8. All of these mesogens have steric substitutions in their central phenyl ring. Importantly, these steric inclusions should be small enough to allow the formation of ferro- and antiferroelectric SmCP or SmAP phases.

The strong polar response of these materials may be attributed to a cooperative behavior of the molecular dipoles organized in 3D ferroelectric clusters in the otherwise uniaxial SmA phase. Such clusters may persist even a few degrees above the clearing point giving rise to a strong current response, occasionally observed in the isotropic phases. Electric field

<table>
<thead>
<tr>
<th>SmAP$_F$</th>
<th>SmAP$_A$</th>
<th>SmAP$_{pa}$</th>
<th>SmAP$_2$</th>
<th>SmAP$_R$</th>
</tr>
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<tbody>
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<td><img src="image4.png" alt="Diagram" /></td>
<td><img src="image5.png" alt="Diagram" /></td>
</tr>
</tbody>
</table>

Fig. 7 Five possible arrangements, and tentative structural names of non-tilted and polarly ordered layered systems. The first sub-column shows a side view where one schematic molecule presents molecular orientation in a single layer. In the second sub-column the corresponding polarization vector is given as seen from above.
dependence of the SHG signals was measured by Shimbo et al.\textsuperscript{69} on both planar and homeotropic cells. The dependence could be modeled by assuming Langevin-type interactions of clusters of dipole moments with electric field. The field of the experimental data gave a cluster size of 210–230 molecules with the dipole moment of 700D in compound from ref. 66. In addition to the field induced SHG signal, in-plane electric fields applied in homeotropically aligned samples can induce biaxiality.\textsuperscript{69} Later, a uniaxial phase has been found showing a threshold behavior of the SHG signals in electric fields.\textsuperscript{76} This antiferroelectric type behavior was explained by the existence of randomly distributed antiferroelectric clusters in the field-free state. Upon the application of an electric field, alignment of the clusters occurs followed by a switching of polarization in the clusters. This orthogonal uniaxial phase with randomly distributed antiferroelectric clusters was designated as SmAP\textsubscript{AR}.

Recently a bent-core compound that undergoes reversible electric field-induced biaxial to uniaxial transitions was also reported. It was explained by an antiferroelectric to ferroelectric transition, where in the intermediate uniaxial state the directors in the neighbor layers are perpendicular to each other. Bent-shaped liquid crystals exhibiting partial double-layer SmA\textsubscript{DP} and SmA\textsubscript{DP\textsubscript{A}} phases have also been described.\textsuperscript{72} Studies on a 4-cyanoresorcinol bisbenzoate compound showed a whole sequence of orthogonal phases SmA-SmA\textsubscript{S}-SmA\textsubscript{APR}-SmA\textsubscript{AP}.\textsuperscript{72} In the helical SmA\textsubscript{S} phase, the polar director is uniformly rotating through a fixed angle $\phi$.\textsuperscript{72} Upon application of the field, the SmA\textsubscript{S} structure first transforms into a bilayer SmAP\textsubscript{A} phase where the polarizations in two adjacent layers are aligned at a right angle.

Field induced tilt of mesogens [electroclinic effect] is usually observed in the SmA\textsuperscript{*} phase formed by chiral rod-shaped mesogens. This effect is attributed to a linear polar coupling between the tilt and polarization allowed in chiral phases. An example of achiral field induced tilt was found in the SmA and SmC phases of achiral bent-core and hockey stick mesogens, respectively (Fig. 9).\textsuperscript{68} This quadratic electroclinic effect is attributed to a biquadratic coupling between the tilt and polarization. Although the biquadratic coupling term is also present in models of rod-shaped mesogens, in BLC it was found to be two orders of magnitude larger, in accordance with the fact that bent-core molecules tend to pack in a polar fashion more than calamitic mesogens. In contrast to linear electroclinic effect, the field-induced tilt occurs above a threshold voltage, which decreases as the temperature reaches the SmA/SmC transition point.

3.B Tilted smectic phases

The majority of the SmCP phases show antiferroelectric ground states\textsuperscript{56,55,56} because typically they have large layer polarizations ($P > 2$ mC m$^{-2}$), which favour an antiferroelectric arrangement, due to dipole–dipole interactions. The antiferroelectric (AF) arrangement can be easily switched to the ferroelectric (FE) by applying external electric fields of typically larger than 3–5 V $\mu$m$^{-1}$ and $f < 10$ kHz. Textures of the racemic SmC\textsubscript{P}A phase usually consist of fan-shaped domains decorated with a few micron wide stripes, attributed to oppositely tilted synclinic domains.\textsuperscript{56} The homochiral SmC\textsubscript{P}A and racemic SmC\textsubscript{P}R structures are anticlinic and the optical axis is parallel to the
layer normal, regardless of the handedness of the domains, and the direction of an applied electric field. The homochiral FE state is synclinic (SmCsPF), and the optical axes make angles \( \pm \theta \) with the layer normal, depending on the sign of the electric field. Structures of the racemic and homochiral phases are illustrated in Fig. 10a and b, respectively.

In addition to compounds showing ferro- and antiferroelectric switching, materials with multistage ferrielectric-like switching were also found in bent-core 2-methyl-1,3-phenylenediamine derivatives.\(^{78}\) There the field-free state is anticlinic antiferroelectric, but transition into the ferroelectric synclinic state occurs via an intermediate ferrielectric state characterized by a repeating three-layer unit with synclinic tilt and parallel alignment of the molecular bows in the first two layers, and anticlinic and antiparallel between the second and third layers. The multistage switching mechanism is due to a frustration imposed by the competition between the long-range dipole–dipole interactions, favoring antiparallel alignment of the dipoles, and steric interactions, promoting a synclinic interlayer interface.\(^{79}\) Until now no field-free ferrielectric phase has been found in bent-core liquid crystals.

Although in the majority of the bent-shape smectics the chirality is conserved while switching between the AF and FE states, in some materials strong fields cause a gradual change of the layer chirality.\(^{80}\) Both the opaque racemic AF and the transparent chiral AF states can be stable and can be interchanged,\(^{81,82}\) or the sign of the layer chirality can even be flipped.\(^{83}\) Racemic domains can be rendered chiral by surface interactions, too.\(^{84,85}\) As pointed out by Lansac et al.,\(^{47}\) the synclinic SmCsP\(_A\) structure enables out-of-plane fluctuations, thus increasing the entropy and decreasing the free energy. This effect becomes less important at lower temperatures, explaining that the synclinic phases often transform to the anticylindrical SmCsP\(_A\) state on cooling, or appears first in heating.\(^{49,50}\) The field-induced switching between racemic and chiral states was explained based on the notion that the synclinic state is more stable.\(^{87}\) Accordingly, when a field strong enough to switch to the ferroelectric state is applied for an extended time, the material prefers to be synclinic, which is chiral. The transformation was facilitated by the application of alternating square wave fields. After field removal this chiral state becomes antiferroelectric and anticlinic, so it can be only metastable. The more stable racemic state can reform either by a nucleation process, or it can be driven back to the synclinic racemic state under triangular electric fields, because during repeated switching it stays longer in the antiferroelectric than in the ferroelectric state.\(^{87}\) All these chirality transformations mean that during the switching, the molecules do not strictly rotate about the layer normal on the tilt cone, but, to some extent, they also rotate around their long axis.\(^{88-90}\) The rotation of the director around the tilt cone preserves the layer chirality, whereas during rotation around the long axis the chirality changes signs. This rotation is faster than the rotation around the cone, and is permissible only in racemic domains. Indeed, it is usually observed that racemic switching is faster than chiral switching.\(^{88}\)

In the case of achiral rod-shape molecules one does not expect any optical activity, but an interesting question is
whether we can have optical activity in bent-shaped materials with homochiral layer structures. Observing bent-core liquid crystals between slightly uncrossed polarizers, it is indeed often found that the texture splits into darker and brighter domains. For polarizers uncrossed in the opposite sense the darker and brighter domains exchange, but for crossed polarizers they have the same brightness. This shows optical activity with optical rotation of 0.1–1 deg μm⁻¹. Except for the example demonstrated in ref. 94, optical rotations were seen only in optically isotropic samples, although not all optically isotropic samples show observable optical rotation. This optical activity might be the result of twisted or propeller shape molecules as illustrated by Earl et al. An alternative model was proposed by Ortega et al. by modeling the SmCₐPₐ with a locally achiral dielectric tensor, where the optical axis is rotating with a pitch of two layers. This model can also lead to an observable optical rotation, indicating that there might be no need for the concept of conformation chirality to explain the optical activity observed in the fluid tilted smectic phases. On the other hand, experiments on birefringent SmCₐPₐ samples showed that the size of the domains with opposite optical rotation is typically in the range of 100–300 μm, whereas the size of domains with uniform layer chirality is an order of magnitude smaller, and the domain boundaries do not even correlate with those of a different layer-chirality. This challenges the layer-scale chirality concept, or indicates another possible mechanism, such as the conformational chirality.

Of course, chirality can also be introduced when one or more chiral carbons are incorporated in the molecules. In some cases the handedness of the homochiral structures was found to be very sensitive to chiral dopants, or to chiral surfaces. However, racemic layer structures may also be formed by enantiomeric chiral molecules, indicating that the molecular chirality has no or minor effect on the overall layer chirality, and can lead to bias of only the otherwise degenerate tilt directions. Concerning the polar order, in addition to the layer polarization Pₑ due to the closed packing of the bent-shaped molecules, another polarization component

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**Table 1** Orthogonal views of SmCP phase of non-chiral banana-shaped molecules viewed in the tilt plane of the antiferroelectric (AF) antiferroelectric and (FE) states (left and right columns respectively). The "polar plane" contains the layer normal and the layer polarization $\vec{P}$, whereas the "tilt plane" is perpendicular to $\vec{P}$. The molecular plane is tilted with respect to the layer normal. The single dashed line (---) indicates syncinic interfaces in anticlinic state, whereas double dashed lines (-----) represent defect walls separating syncinic layers with opposite tilt directions. (a) Racemic states and (b) homochiral states.

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![Fig. 10](image-url).
P₂, due to the chiral and tilted molecular structures, may exist. In the antiferroelectric racemic domains, P₂ averages out but, due to the synclinic order and the molecular chirality, a P₁ normal to the tilt plane, such as in the calamitic SmC* phase, is possible. On the other hand, in the anticlinic ferroelectric state P₁ vanishes, leaving only a P₄. For binary mixtures of an achiral and chiral bent-shape materials P₁ could be measured and is found to be an order of magnitude smaller than P₄. This result makes sense, since P₁ is a secondary order parameter (due to tilt), whereas P₄ is a primary order parameter.

Experimental evidence for the SmCTP (SmC₄) phase was found both in free-standing films and in bulk samples. According to certain models, they can be identified with the switchable B₇ textures exhibited by many derivatives of 2-nitro- and 2-cyano-resorcinol. The B₇ texture is the characteristic growth of spiral and other helical domains obtained on slow cooling of the isotropic liquid. The non-switchable B₇ materials usually have a columnar structure. The switchable B₇ materials are mainly ferroelectric, although a few examples for antiferroelectric structures were also found. In some cases a transition between ferroelectric and antiferroelectric phases has been seen. In the homologue series of symmetrical bent-core compounds containing terminal n-alkyl carboxylate groups, an interesting odd-even effect was found. When n is an odd (even) number, anticlinic (synclinic) structures are formed. This effect probably has entropic reasons; for an odd number of carbon atoms the end segments of the neighbor molecules are parallel to each other when the tilt of the molecular planes are anticlinic, whereas for the even numbers the end segments are parallel in the synclinic situation.

In the case of achiral bent-core molecules, where the value of polarization is not determined by the tilt, one would not expect an electro-clinic effect. In fact the opposite of the electro-clinic, namely a field-induced suppression of the director tilt was observed in 1,3-phenylene bis[3-fluoro-(4-n-octyloxy-phenyliminomethyl)benzoate] (PBFOB). It was found that high electric fields eventually lead to a meta-stable phase with zero director tilt. The tilted phase slowly recovers at low fields. It was proposed that the field-induced quenching of the layer fluctuations is responsible for the observed “dis-clinic” effect.

4 Modulated smectic structures

Decoupling between the tilt and polarization in bent-core liquid crystals allows for a linear polarization splay term in free energy density. The molecular origin of this term is believed to be due to a mismatch between the volume of the central core and the terminal groups of the mesogens.

As a full divergence term, the polarization splay affects the anchoring of the molecules at the boundaries of the liquid crystalline domains. In a ferroelectric smectic phase, as the coupling strength increases, the state with a uniform director becomes unstable to nucleation of defects, which is favored by the polarization-splay term. A resulting state represents a striped phase formed by the polarization-splayed domains separated by defect walls.

4.A SmCPmod

Most of the smectic phases have one-dimensional periodicity, i.e., their X-ray pattern can be indexed by one parameter, the layer spacing d. However, by synchrotron X-ray scattering a large number of materials have been found to have layer-modulated structures in their tilted SmCP or SmC₉ phases, which require two lattice parameters, a and b, and a vertex angle γ to index their X-ray pattern. The reason for the layer modulation is a chiral symmetry-breaking coupling between the polarization splay described above, and the tilt of the molecular planes with respect to the layer normal k. At the boundaries of the stripes, where the splay is reversed, the tilt becomes reduced which results in a strain driving undulation of the smectic layers. In the case where the layers remain continuous, polarization modulated (PM) and layer undulated (LU) phases occur. Different combinations of the tilt and polarization directions in the adjacent splay stripes yield various structures, such as synclinic SmC₉mod and anticlinic SmC₉mod phases.

4.B SmAPmod

Layer modulated non-tilted structures were not expected, because the modulation requires local layer dilation. However recently there was a report about a material with the SmAPmod SmAP₉ phase sequence showing an unusually high elastic modulus attributed to the polarization stiffening of the bend elastic constant. In this case the layer dilation might be possible due to interdigitation, or local uncorrelated tilt, or not fully stretched aliphatic chain configurations. Interestingly the SmAPmod phase also showed a bistable electric response, similar to what has been described earlier.

Very recently the chemical synthesis and physical measurements on a strongly anisotropic bent-shape liquid crystal
material showing a layer undulated structure in an apparently non-tilted ferroelectric phase similar to that observed by Zhu et al.\textsuperscript{141} was also reported.\textsuperscript{143} In this case, however it appears below an SmCPF\textsubscript{mod} phase, and the analysis of the measurements led to the conclusion that the observed lower temperature layer undulated phase is rather an SmTP than an SmAPF\textsubscript{mod} phase, and the physical mechanism of the undulation is different from the mechanisms described earlier.

4.C Dark conglomerates

The SmC\textsubscript{A} phase of the bent-shape molecules may become optically isotropic and show optical activity if the opening angle is near 109°, and the tilt angle is close to 45° (ref. 94) In contrast to this special SmC\textsubscript{A} phase, a number of materials, showing the local SmCP structure, possess a short (\textasciitilde100 nm) smectic correlation length, indicating a disordered phase structure.\textsuperscript{144} Such a mesophase, designated as “Dark Conglomerate” (DC), is also optically isotropic and may show optical activity. Spontaneously formed chiral domains of opposite handedness can be visualized in depolarizing microscopy with slightly uncrossed polarizers, as shown in Fig. 11.

Molecular structures of typical compounds with the DC phase are shown in Fig. 12.

The behavior of the DC phase was studied in detail by several groups.\textsuperscript{145,150–153} It was found that under the action of an electric field, or depending on the thermal history of the sample, the isotropic texture occasionally transforms into a birefringent one. The liquid crystal remains in this state even after the removal of the field showing an electrooptical switching to the ferroelectric state, characterized by a strong current response and SHG activity. Sometimes the opposite effect occurs: the chiral isotropic state is induced by an exposure to a strong DC electric field\textsuperscript{150} or by slow cooling from the isotropic phase.

**Fig. 12** Chemical structures and phase sequences of various compounds showing dark conglomerate phases; (a) ref. 144 and 146, (b) ref. 144, (c) ref. 147, (d) and (e) ref. 148, (f) ref. 97 and 98 and (g) ref. 144.

**Fig. 13** Freeze-fracture TEM images of the DC phase of compound GDa226. The figure is reproduced from ref. 144 with the permission of AAAS.
under a square-wave AC field. The field-induced chiral isotropic phase shows a bistable switching between the domains of opposite chirality. This switching process occurs without any detectable birefringence and is accompanied by a current response with switching polarization as high as 300 nC cm$^{-2}$. The twisting power of the chiral domains can be as large as 0.1° per micron. The structure of the DC phase was established by several groups by using X-ray diffraction and freeze-fracture transmission electron microscopy (FFTEM). These studies revealed characteristic 20–100 nm size domains of saddle-splay type layers with a hexagonal long-range order (Fig. 13). DiDonna and Kamien showed that the energy cost of layer deformation could be compensated by the gain of the Gaussian curvature of the surfaces when the saddle-splay elastic constant $K_{24}$ is negative. This can explain the occasional occurrence of the optically inactive DC phases.

The saddle-splay curvature of the layers is also believed to contribute to the large optical activity of the phase, which cannot be explained by the layer chirality of the tilted polar phase alone. In an earlier model of random oriented smectic domains, the formation of the chiral domains and their optical activity was attributed to nano-segregation of chiral SmC$_A$F$_A$ domains.

4.D Helical nanofilament phase (HNF)

The so-called B$_4$ phase (the 4th phase found chronologically among bent-shape liquid crystals) forms at low temperatures in many bent-core materials and their mixtures with rodlike mesogens. The B$_4$ phase has a blue reflection color, and it is almost optically isotropic (Fig. 14). Similar to the DC phase, in sandwich cells domains of opposite handedness can be distinguished by their optical activity with the rotatory power of the order of 1° μm$^{-1}$.

Although no electrooptical switching could be found in this phase, it is SHG active, indicating a polar order on a micrometer length-scale. The strong electrogyration effect (the chiral Pockels effect), observed in B$_4$ materials, is promising for applications. Although first a structure similar to the TGB phase was suggested, X-ray diffraction showed a local layer structure with a short correlation length in the range of 40 nm. Detailed studies, using freeze-fracture transmission microscopy (FFTEM) and electron diffraction (ED), revealed that the B$_4$ phase is formed by chiral twisted nanofilaments. It was shown that the competition between the smectic layering and chirality-induced twist results in a frustrated state with a suppressed layer structure and twisted filaments separated by chirality. Each molecular arm can be viewed as an elastically isotropic slab that dilates parallel to and compresses perpendicular to the molecular tilt direction as a result of the hexagonal in-plane ordering. Because the tilt directions of the top and bottom molecular arms are orthogonal, the two elastic slabs adopt a saddle-splay curvature to relieve the intralayer mismatch. The local layer chirality, which is determined by the polarization

![Fig. 14](https://example.com/fig14.png) Microphotographs showing the B4 phase: (a)–(c) pure P-8-O-PIMB at 30 °C and (d)–(f) a mixture of P-8-O-PIMB with 20 wt% 5CB at 137 °C.
and molecular tilt, results in distinct regions with orthogonal saddle-splay and opposite signs of filament twist.

In recent years, mixtures of the bent-core materials with rodlike mesogens such as 5CB or 8CB have attracted particular attention, because, due to a strong chiral nano-segregation, the mixtures show large homochiral domains, thus enabling direct observation of the filament nucleation and growth. The studies have shown that the small rodlike mesogens often become segregated on a nanoscale and embedded into the network of helical nanofilaments formed by bent-core mesogens (Fig. 15a and c). Such mixtures show a remarkable thermal behavior, reflecting the distinctive dynamics of the bent-core nanofilament network and the embedded nano-segregated phase of rodlike mesogens.168-170

5 Polar columnar phases

The chronologically first observed phase of bent-core molecules (B1) in films has mosaic textures and circular pseudo-broken fans and shows nearly no electro-optical switching. It is characterized by a complex small angle X-ray scattering (SAXS) pattern, which can be indexed by a 2D structure, which means a columnar phase.171 The columns of frustrated blocks consist of 4 or 5 molecules, resulting in an overall antiferroelectric structure with p2mg symmetry. Later, however, several different types of columnar BLCs were found which showed various symmetries with ferro- and antiferroelectric orders and electro-optical switching.26,27,114,171,172 The major difficulties with the p2mg model of the columnar phases were the absence of the cross-reflections, 21, and the often observed splitting of the diffuse scattering, which results from the molecular tilt.174 These difficulties have led to a model, where the bows of the molecules align along the columns giving rise to a so-called reversed B1 phase (B1rev) (Fig. 16b-d). There are several types of reversed phases: an orthogonal phase B1rev with pmmn symmetry, and a tilted B1rev tilted phase with p11n symmetry. In contrast to the B1 phase, the B1rev phases show electro-optical switching in strong fields (E > 15 V μm⁻¹) associated with a strong polarization switching as high as 700 nC cm⁻², comparable to that of the SmCP phase.

In a compound shown in Fig. 17a the B1 phase was characterized by an orthorhombic non-tilted centered cell with the cell parameters a = 50 Å and 80 Å < b < 90 Å. To explain the occurrence of the SAXS peak indexed as 22, it was suggested that the polarization in the columns shows a spontaneous splay173 (Fig. 16c) similar to the layer modulated SmCPmod structures. A rich variety of columnar phases were also found in silylated naphthalene derivative bent-core compounds (see Fig. 17).168 While asymmetric mesogens with a single silyl terminal group show smectic phases, symmetric mesogens with two silyl groups exhibit a series of ferro- and antiferroelectric columnar phases with an oblique lattice structure. It is the sterically frustrated silyl groups, which are thought to disturb the layer order and favor a columnar structure. Polarization switching measurements usually show smaller values of the polarization and higher threshold fields (>35 V μm⁻¹) in the columnar phases than in ferroelectric SmCP phases.168

Although most of the phases discussed above are characterized by a rectangular lattice, Gorecka et al.175,177 found a different type of columnar phase in an achiral bent-core mesogen with branched terminal chains (Fig. 18a and b). In addition to a rectangular Colh phase, this compound exhibits two hexagonal columnar phases: a non-switchable Colh phase...
and an antiferroelectric ColhPₐ. The structure of the columns is formed by flat disc-shaped (Colh) and cone-like (ColhPₐ) aggregates of four mesogens (Fig. 18c and d). Due to an asymmetry of the electron-density distribution, a spontaneous dipole moment of the columns occurs in the cone-shaped configuration.

A transition between the disc-shaped and cone-shaped configurations gives rise to a new relaxation soft mode, where the direction of the cone tip oscillates. This mode is designated as “umbrella mode” and it yields a new switching mechanism of the columns shown in Fig. 18, which was unambiguously confirmed by SHG interferometry measurements and dielectric spectroscopy.¹⁷⁷

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Fig. 17 Selected mesogens showing columnar phases: (a) P-n-O-PIMB compound showing the B₁ phase;¹⁷¹ (b) a compound with the reversed and reversed tilted B₁ phases;¹⁷₁ (c) a compound with a splay-polarization B₁ phase;¹⁷₁ (d) a silylated naphthalene derivative compound showing a range of ferroelectric and antiferroelectric columnar phases;¹⁶₉ (e) a polycatenar compound showing polar hexagonal columnar phase formed by disc- and cone-shaped molecular agglomerates;²⁷ (f) a compound showing columnar phases with local triclinic symmetry.¹₄₄

Fig. 18 (a) Schematic drawing of the column cross-section made of four bent-shaped molecules; (b) in the ColhPₐ phase, the molecules form a cone-like structure with non-compensated dipole moment depicted by an arrow, (c) a schematic illustration of the polar switching in the Colh phase of polycatenar molecules and (d) temperature dependence of SHG intensity in the Colh and ColhPₐ phases of polycatenar molecules with n = 12 and 16. Insets show the P–E hystereses. Figures (a) and (b) reprinted with permission from ref. 217. Copyright 2011 American Chemical Society. Figures (c) and (d) are reproduced from ref. 216. Copyright 2006 Royal Society of Chemistry.

628 | Soft Matter, 2013, 9, 615–637

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6 Other structures

6.A Freely suspended films

Freely suspended smectic films present an excellent system to study the mesophase behavior of smectics and phase transitions in quasi two-dimensions. Stable films are usually formed by smectic and some columnar liquid crystals. Quantized thickness and perfect alignment of molecular layers are distinguishing features of the freely suspended films making them indispensable for investigation of polar order, elastic and rheological properties of liquid crystals using optical microscopy, ellipsometry and X-ray. In particular, the direction of the molecular tilt and polarization can be determined by means of depolarized light microscopy at an oblique incidence. Very small residual (spontaneous) polarization can be detected in films due to a dipolar coupling of the polarization with an external electric field. This coupling gives rise to the $2\pi$ director inversion walls indicative of the polar order.

In earlier studies, synclinic antiferroelectric organization of the molecules of the SmC$_{SP}A$ phase was established in freely suspended films. Antiferroelectric films were distinguished by a strong odd–even effect where the residual polarization was aligned along the tilt director in films of an even number of layers and perpendicular to tilt director otherwise. It was shown that the antiferroelectric order of the layers extends down to the thickness of two molecular layers, followed by a breaking of layer chirality.

In freely suspended films, the development of the long-wavelength polarization-modulated state is accompanied by the formation of labyrinthine textures formed by edge dislocations (Fig. 19). One example of such instability was found in compounds showing an SmCP$_A$ and an SmCP$_{mod}$ phase. It was shown by SHG that this instability is preceded by an antiferroelectric-ferroelectric phase transition. In the ferroelectric phase, the instability is accompanied by the nucleation and growth of string-like defect lines separating the stripes of splayed polarization. The instability initiates a reversible re-organization of the edge dislocations in films of inhomogeneous thickness, leading to an intricate maze pattern formed by terraces of the layer steps.

A different type of string structure was found in films in the SmCP$_F$ phase. Those strings separate the regions of opposite bend deformation of the molecular tilt director, while both the tilt direction and the direction of the spontaneous polarization remain continuous (Fig. 20a). This kind of instability, characterized by a continuous director field, is different from the polarization splay instability, as there is no preferred sign of the splay of the polarization vector (bend of the $c$-director). Formally, this instability can be described by the sign inversion of the bend elastic constant $K_b$. The sign inversion of $K_b$ in bent-core nematics has been discussed, but the molecular mechanisms underlying this instability remain unclear. Interestingly, in mixtures of rod-shaped and bent-shaped LCs, only a strong reduction of $K_b$ has been found experimentally.

Another peculiarity of freely suspended films formed by bent-core mesogens is the occasional occurrence of films showing a very small residual polarization, and no polarization...
in bulk. This phenomenon was found in earlier studies of the antiferroelectric SmCP phase of bent-core mesogens, and in the paraelectric SmC phase of achiral hockey-stick mesogens. A clear indication of a weak residual polarization \( P_s = 1.8 \, \text{nC cm}^{-2} \) was the behavior of the \( 2\pi \) inversion walls of the director. The non-dependence of \( P_s \) on the film thickness excludes the surface-induced polarization typical for the antiferroelectric phases. In a chlorine-substituted bent-core compound, the origin of this weak spontaneous polarization is not understood yet. Although it seems that the steric interactions are still important, the occurrence of the weak spontaneous polarization becomes geometry dependent. In the case of bulk antiferroelectric phase, the residual polarization might originate from a weak helicity of the antiferroelectric structure.

For other materials with a paraelectric phase a different stabilization mechanism of the ferroelectric state should be possible.

### 6.B Freestanding fluid fibers

Surface tension tends to minimize the surface area/volume of a fluid; therefore, Newtonian fluid fibers (described by a constant viscosity) are stable only if their length is smaller than their circumference, i.e., their aspect ratio \( L/D < \pi \) (Rayleigh–Plateau instability). Longer fibers can be drawn only from non-Newtonian fluids that harden during the pulling process. The hardening can be achieved either by cooling, such as in glass fibers, or by solvent evaporation, like when spider silk loses water after spinning. Freestanding, three-dimensional slender fluid filaments are never stable, except in some liquid crystals with reduced fluid dimensionality, such as in columnar phases that can be considered as one-dimensional fluids. Columnar liquid crystalline phases of disc-shaped molecules were found to form stable filaments with up to 0.2 mm length and 1.5 \( \mu \text{m} \) diameter. Their stability is due to the large compression modulus of the columns. Low molecular weight liquid crystals comprised of rod-shaped molecules do not form fibers, and it has been observed that nematic and smectic A bridges collapse at aspect ratios of \( R = \pi \) and at \( R = 4.2 \), respectively. Smectic liquid crystals formed by rod-shaped molecules generally form thin films, however tilted smectic phases of bent-core liquid crystals (to some extent even the nematic...
phase) were found to form stable and slender filaments (see Fig. 21).\textsuperscript{5,131,190} In stable freestanding fibers the structure is axially symmetric with layers wrapping cylindrically around the core.\textsuperscript{131,190} Such a structure mimics the columnar phase, and stabilizes a liquid crystal cylinder against the Rayleigh–Plateau instability.\textsuperscript{5,131,191} Since in this geometry the molecules can still flow inside the layers, such filaments combine the stability of solid fibers with the fluidity of a quasi one-dimensional liquid channel. These properties allow precise measurements of the optical, electrical, rheological and electro-mechanical properties of BLC fibers and freestanding bridges. In addition to single filaments, a number of larger filament bundles can be also formed with diameters of 10 μm or larger with aspect ratios greater than 100. The most stable BLC filaments may remain stable until the radius decreases below 1.5 μm.

Dynamical properties of freely suspended liquid crystal filaments have been explored and provide information on filament tensions and damping processes.\textsuperscript{83,131,190,192–201} Recently, new methods for the mechanical characterization of the filaments, based on static deformations, have been proposed.\textsuperscript{191,193,194,201–203} BLC filaments can mechanically respond to electric fields:\textsuperscript{190} in their single strand forms they show a transversal vibration with the frequency of the electric field applied along the fiber axis (see Fig. 22a), and in their multi-strand bridge form they flow along the field as shown in Fig. 22b. Both of these electromechanical effects indicate the polar nature of the fibers and offer their use as micro-electromechanical devices.

A theoretical study of the equilibrium size of single freestanding smectic filaments found that the stability of the filament increases in the SmC\(_d\) phase.\textsuperscript{204} It was shown that frustrations in molecular packing generated by molecular substitutions and electrostatic potentials necessitate a local C\(_3\) symmetry and lead to a spontaneous polarization splay and layer bending in BCLCs that are responsible for the stability of the filaments.\textsuperscript{204} More complicated scenarios were also discussed mathematically.\textsuperscript{204} The stability of SmC\(_{mod}\) fibers has been recently explained as the result of a periodic pattern of defect boundaries, which decorate molecular layers of the liquid crystal.\textsuperscript{205}

### 6.C Ferroelectric nematic phase

In the nematic phase of bent-shape molecules the translational symmetry is frustrated, and the molecules tend to stick together locally into temporary periodic (smectic-type) clusters. In this case the nematic order is allowed only in a length scale much larger than the size of the clusters. 3D nematic phases with a spontaneous macroscopic polarization pose a challenge to both theoreticians and experimentalists working in the field of liquid crystals. Although polar nematics were predicted theoretically, the stability of these phases remains controversial. Symmetry-allowed twist and splay instability may destroy the polar structure and cancel the macroscopic polarization. Bent-core nematic materials are found to be dielectric and no polarization current peak is usually seen when the electric current is measured through the sample under triangular electric fields.\textsuperscript{297} Recently, however, Francescanzari\textsuperscript{elli} et al.\textsuperscript{286} reported a ferroelectric-type electric current response, in a very high temperature nematic phase at low frequencies (1–2 Hz) (see Fig. 23a). Although the area of the current peak seems to decrease considerably in the isotropic phase, one needs to be careful while interpreting the current peak as a sign for polarization reversal, as at such low frequencies one can observe very similar current peaks even in simply dielectric liquid crystals, such as 5CB, as we show in Fig. 23b. Although the current response peak found in 5CB is sharp, its shape differs from that found in ferroelectrics. The rising part of the curve is steep and the decay is slow, which is opposite to what one usually finds in ferroelectric smectic materials, because the switching rate of the polarization is increasing at increasing fields.

Very recently a similar ferroelectric-type polarization peak was observed for a novel 3-ring bent-core nematic material\textsuperscript{155} even at higher frequencies (\(f = 12\) Hz). The peak there did not disappear at the N–I transition, but only gradually decreased and vanished only at temperatures about 12 °C higher. The origins for these current peaks in bent-core nematics and in other phases are under investigation.

### 6.D Solid ferroelectrics

Most solid ferroelectric materials are inorganic and only a few organic ferroelectric materials are known. Apart from several examples of polymer-based solid ferroelectrics, there are only a dozen low-molecular weight ferroelectric compounds.

Bent-core materials of molecules with a strong steric moment and possessing bulky groups enable the formation of solid or glassy polar, and in some cases, even switchable materials. Weissflog \textit{et al.} demonstrated ferroelectric and pyroelectric properties in five-ring compounds synthesized by esterification of 2-methylresorcinol with two equivalents 4-((4-n-hexadecyloxy-phenoxyl)benzoic acid.\textsuperscript{286} It was found that the principle underlying the polar properties of the mesophases formed by bent-core mesogens can also be expanded to the crystalline state.

### 7 Possible applications

Although to the best of our knowledge there is no commercial device yet that would contain bent-core ferroelectrics, there are numerous physical phenomena that offer practical applications. A short list of the most promising effects and their possible uses follow.

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\( \text{Fig. 24} \) Electrically switchable light shutter based on switching between SmCaPA and SmC\(_{mod}\) states of non-chiral banana-shaped molecules. Pictures illustrate 1 cm\(^2\) areas of a 10 μm thick film at room temperature. At zero fields the film is transparent (LEFT) and the text ‘ALCOM’ placed right behind the cell is visible. At fields \( Е > 8 \text{ V μm}^{-1} \) the film is opaque and the text is blurred (RIGHT).
chiral AF states were found to be stable and interchangeable, where the layer chirality was changed gradually with strong fields. This implies their use in optical storage devices, or multi-stable electronic devices, such as e-books, that use energy only during retransformation between chiral and racemic states.

In addition to these promising light scattering properties, anticlinal and synclinic domains also differ in their birefringence. Anticlinic domains have a small birefringence ($\Delta n_a < 0.05$) since typically the tilt angles are large ($\theta > 30^\circ$), whereas synclinic domains have a birefringence comparable to that of calamitic molecules ($\Delta n_s > 0.1$). It was observed in materials with a large tilt angle ($\theta \sim 45^\circ$) and small opening angle ($\Phi \sim 110^\circ$) (ref. 161 and 166 that the anticlinic state was basically optically isotropic ($\Delta n \sim 0$). This optical isotropy offers an excellent dark state with a large viewing angle.

Bent-core SmAP$_{nD}$ and SmCaP$_{nD}$ materials in their homeotropic textures (layers are parallel to the substrates) are uniaxial at zero fields, but with in-plane fields they can be switched to biaxial states. In this case, the OFF state is dark between crossed polarizers, while the field-induced biaxial state becomes birefringent with the optical axis perpendicular to the electrodes. This situation in the SmAP$_{nD}$ phase is shown in Fig. 25.

7.B Non-linear optics (NLO)
Ferroelectric phases of bent-core molecules possess higher effective non-linear optical coefficients than rod-shaped molecules, which may qualify them to be important for optical processing, such as the development of new lasers, optical filters in photonics and telecommunication. They can be considered as an alternative to NLO nematic polymers because the latter needs very strong electric fields to achieve the polar order required. Importantly, bent-core liquid crystals allow for a significant component of the hyper-polarizability along the polarization direction, and it was concluded that the bent molecular shape is favourable for a correct design of NLO materials, although in order to improve large NLO efficiency, p-bridged systems linked to enhanced electron donating and withdrawing groups must be incorporated. We note that the conditions for the second harmonic generations are exactly the same as for piezoelectricity; therefore it is not surprising that piezoelectric responses indeed have been observed in a ferroelectric SmCP$_4$ material.

7.C Optical wave guiding of fibers
Recently it was demonstrated that smectic filaments of bent-core materials can guide light coupled into one end of a polar bent-core smectic filament. These filaments represent the first optical fibers with an anisotropic refractive index that is uniaxial with the optical axis along the fiber axis. For applications in telecommunications, one needs to decrease the absorption of the molecules in the infrared range, which can be an interesting challenge in chemistry.
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