Structural studies on different types of ferroelectric liquid crystalline substances

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Abstract

Structural studies of ferroelectric liquid crystalline substances of different molecular structure have been reviewed. The discussion of the results deals mainly with the structure of chiral liquid crystals forming the smectic mesophase with ferroelectric order, as the research on ferroelectric liquid crystals, due to their high potential for application in electro-optics and photonics, has recently become one of the most attractive fields. Based on data of polarizing optical microscopy and X-ray diffraction obtained for unoriented samples we have identified the type of the mesophases, the temperature of the phase transitions and outlined the phase diagrams. An analysis of the relation between the molecular conformation and different types of phase transitions has been performed. The layer spacing and the average intermolecular distances have been determined for all studied phases from the positions of the small and the large angle diffraction peaks, respectively.

1. Introduction

Structures without mirror symmetry are ubiquitous in nature. This handedness, or chirality, of liquid crystalline molecules has a profound influence on the macroscopic physical properties of these systems, including the appearance of new phases [1]. Indeed, the majority of optical applications of liquid crystals (LCs) are due to chiral structures, namely the thermochromic effect of cholesteric liquid crystals, the optical activity in twisted nematic liquid crystal displays, and the ferroelectric and antiferroelectric switching of smectic liquid crystals.

The rapidly growing demand for ferroelectrics in electronics industry, particularly as fundamental materials for capacitor, display and memory production, requires new functional and advanced ferroelectric materials. Solid-state ferroelectrics exhibiting perovskite

structures have paved their way into memory applications, notably as non-volatile ferroelectric memories (FeRAM), with huge resistance to radiation and tremendous writing speeds. On the other hand, liquid crystalline ferroelectrics (i.e. ferroelectric liquid crystals, FLCs) have found application in flat panel display technologies, competing with other technologies based on nematics like In-Plane Switching (IPS) and Supertwisted Nematic (STN). Ferroelectric liquid crystal displays (FLCDs) may be bistable, i.e. they can retain an image without power; application of a voltage is only necessary to change the image. This leads to substantial power savings, in the order of 75times faster than a standard LCD [2]. The rapid response is essential to eliminate video anomalies when reproducing fast moving video images. FLCDs may have other advantages, such as vivid colours, wide viewing angle and high brightness [3]; moreover they do not need expensive, active switching electronics, thus reducing display costs by the virtue of using simpler, passive matrix switching systems.

2. Classification of phases and their structures

The liquid crystalline state is a state of matter which is characterized by the alignment of molecules or molecular aggregates. Thermotropic liquid crystals consist of rod-like, bent-shaped or disk-like molecules, and show one or several additional phases in the temperature range between the crystalline and the isotropic liquid state. These mesophases are fluid, but anisotropic. Their physical properties depend on the orientation, like the properties of a crystal. The structure of liquid crystalline phases is characterized by a long-range orientational order of the molecules. However, the centres of the molecules are free to move and show either no positional order (nematic phases) or a quasi-long range positional order in less than three dimensions (smectic and columnar phases).

In the early stages of the study of liquid crystals, they were classified according to the degree and the nature of the ordering as nematic, smectics and cholesteric. Thus, from the beginning, the structural studies have played an important role in the investigation of liquid crystals. Like liquids, they retain a considerable degree of disorder; therefore liquid crystalline phases naturally cannot be characterized structurally in the same detail as solid crystals.

The distinctive feature of nematic liquid crystals is that the long axes of molecules are arranged on average in parallel fashion. In smectic liquid crystals, the molecules again are approximately parallel, but in addition they are stacked in parallel layers. The local structure of the cholesteric mesophase is analogous to the structure of the nematic; yet cholesterics possess a gradual twist in the orientation of molecules in space, leading to a helical arrangement, which results in optical activity of this liquid crystalline phase.

There is a considerable variety of the properties and structures of smectic phases. X-ray diffraction is the powerful technique that made it possible to characterize specifically each of the smectic subtypes, namely A, B, C, D, E, F, G, H, I, J and K [4] (see Figure 1 for some examples). In the structural description and classification of "monolayer" smectics, account is usually taken of the nature of the packing of the molecules in the layer, whether or not the molecules lie at an angle to the layer normal, and the presence or absence of correlation between the superimposed layers. Four types of packing of the molecules in the layer are distinguished: disordered, "hexatic" (having only short-range order), hexagonal and herring-bone.
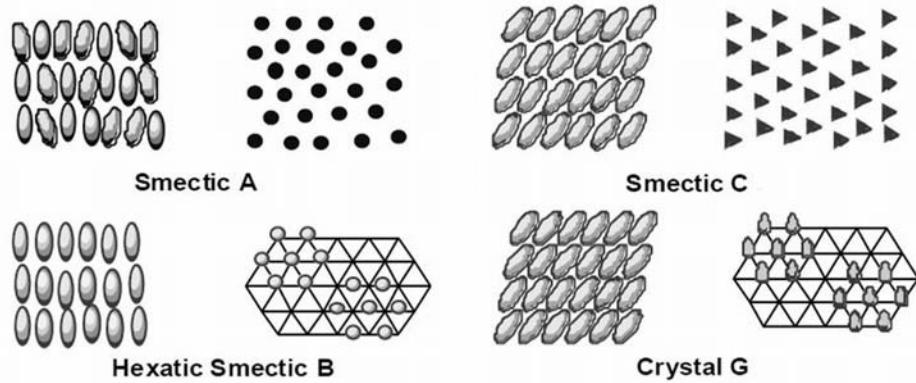
Figure 1. Arrangement of molecules of various smectics [5].

3. Chiral smectic phases and ferroelectricity

Chirality in smectic phases can be introduced in two basic ways: one is to rotate each subsequent monolayer of a SmC* phase (possessing inclined molecules) which gives the chiral SmC* phase with a helical director structure, and another way is to have slabs of an SmA* or SmC* material regularly stacked in a helical fashion along an axis, which is parallel to the smectic layers to give TGBA* or TGBC* (twist grain boundary smectic A* or C*) phase [6-11].
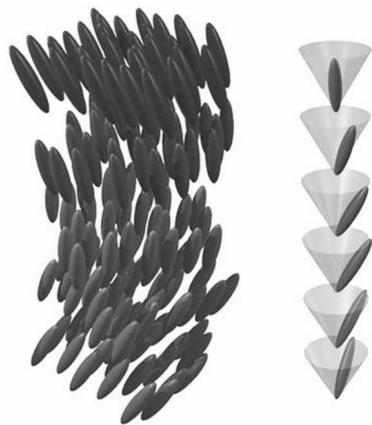

Figure 2. Sketch of the chiral smectic C* phase structure.

Another important implication of chirality is that due to hindered molecular rotation the permanent dipole moments of the molecules do not average out and lead to the appearance of a spontaneous electric polarization in each layer of the SmC* phase. Due to the helical arrangement of tilted molecules in each layer (Figure 2), the vector of spontaneous electrical polarization spirals with the periodicity of the helical pitch around the layer normal. Although we can name these materials *helielectric*, by virtue of their similarity to the ferromagnetic materials the term *ferroelectricity* is commonly used. Additionally, the chiral smectic C* phase can be regarded as an analogue to the mechanically twisted achiral smectic C phase [12].

3.Studies on homologous series

A lot of efforts have been directed to obtain polar liquid crystalline materials that can respond application demands, particularly to prepare ferroelectric mixtures for electro-optic devices and application in photonics. Even more efforts have been directed in order

to understand the relationship between the chemical structure and physical properties of the ferroelectric liquid crystalline materials [13].

We have studied ferroelectric LCs with the 2-alkoxypropionate chiral group, i.e. with one chiral centre [14-15] (Table 1). They have originally been synthesized with the aim to obtain polar liquid crystalline materials that can respond application demands for electro-optic devices. Another objective is to study the effect of the chiral chain length on the mesomorphic and structural properties as well as on the spontaneous polarization of the materials showing a broad temperature range of the ferroelectric phase in order to contribute to a better understanding of the molecular structure - physical property relationship. The phase transition temperatures determined by polarization optical microscopy (Table 2) are the basis for the investigation of unoriented samples by X-ray diffraction. The detailed structural studies of these mixtures allow one to determine the molecular arrangement, conformation and packing, as well as the molecular parameters: the average lateral distance between the long axes of neighbouring parallel molecules, D, and the thickness of the smectic layer, d. These parameters have been obtained using Braggs law from the large angle and the small angle X-ray diffraction peaks, respectively.

Table 1. General chemical formulae of the compounds under study.

$H_{2n+1}C_n O-\bigcirc-\overset{O}{\underset{O}{C}}-\bigcirc-\bigcirc-O-\overset{O}{\underset{\underset{CH_3}{|}}{C}}\overset{*}{C}H-OC_mH_{2m+1}$

H n/m series

$H_{2n+1}C_n O-\underset{CH_3}{\overset{CH_3}{\bigcirc}}-\overset{O}{\underset{O}{C}}-\bigcirc-\bigcirc-O-\overset{O}{\underset{\underset{CH_3}{|}}{C}}\overset{*}{C}H-OC_mH_{2m+1}$

DM n/m series

$H_{2n+1}C_n O-\bigcirc-\overset{O}{\underset{O}{C}}-\bigcirc-O-\overset{O}{C}-\bigcirc-O-\overset{O}{\underset{\underset{CH_3}{|}}{C}}\overset{*}{C}H-OC_mH_{2m+1}$
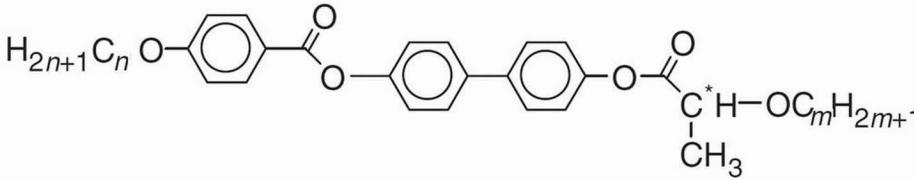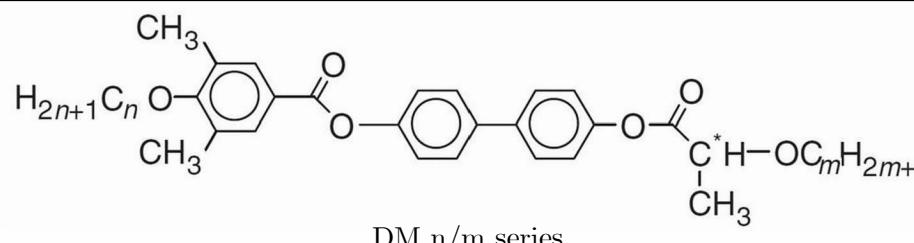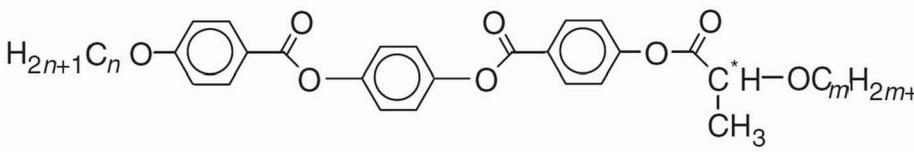
QM n/m series

The molecular conformation determined the type and the temperature of the phase transitions of these compounds. Due to the sterical hindrance of the rotation around the single bond in biphenyl, the inner parts of the H- and the DM- series possess more rigid conformations than the QM-series; this subsequently gives rise to a multitude of phases

(BP, N*, SmC*, SmB*) in these two series, in contrast to the QM-series which possess the N* and SmC* mesophases only.

Comparing the molecules with similar alkyl chain lengths but with different molecular cores (e.g., **H12/10**, **DM10/12**, **QM12/10**), much lower clearing points, as well as other phase transition temperatures are detected for the DM-series than for the H- and QM-series. That can be explained as a result of the presence of the lateral substitution by two methyl groups on the benzene ring far from the chiral centre (see Table 1: DM-series compared to the H-series) which discourages packing in close arrangement; therefore it increases the disorder of molecular packing and hence lowers the phase transition temperatures and makes the phases monotropic.

Lowering the phase transition temperatures shifts the SmC* phase in the DM-series very close to room temperature, unluckily for the price of strong narrowing its temperature range with respect to that of the H- and QM-series.

The same factor, the substitution by two lateral methyl groups, probably additionally twists the molecule itself, resulting in the emergence of a double twisted helical structure - the blue phase - with a moderately wide temperature range of 6.2^{o}C (see Table 2 - **DM 7/10**).

Table 2. Melting points, sequence of phases and phase transition temperatures (^{o}C) for the homologues from H-, DM- and QM-series [16,17].

Comp.	m.p	Cr	^{o}C	SmB*	^{o}C	SmC*	^{o}C	N*	^{o}C	BP	^{o}C	I
H 12/4	84.1	•	80.9	-		•	141.0	•	144.6	-		•
H 12/5	75.0	•	73.5	-		•	136.0	-		-		•
H 12/7	85.3	•	57.9	(•)	(80.7)	•	144.7	•	148.0	-		•
H 12/8	78.2	•	59.5	(•)	(73.0)	•	137.1	-		-		•
H 12/10	78.7	•	57.0	(•)	(63.8)	•	127.4	-		-		•
DM 7/5	68.3	•	30.0	-		(•)	(32.6)	(•)	(54.1)	-		•
DM 7/6	59.9	•	30.0	-		(•)	(35.8)	(•)	(52.6)	-		•
DM 7/10	73.0	•	43.0	-		(•)	(45.4)	(•)	(49.8)	(•)	(56)	•
DM 10/8	62.3	•	38.0	-		(•)	(49.1)	(•)	(53.1)	-		•
DM 10/12	74.0	•	51.5	-		(•)	(55.7)	-		-		•
DM 12/12	73.9	•	42.8	-		(•)	(57.0)	-		-		•
QM 10/10	98.0	•	84.0	-		•	128.0	•	135	-		•
QM 12/9	99.0	•	86.0	-		•	129.0	•	131	-		•
QM 12/10	98.0	•	86.0	-		•	131.0	•	132	-		•

() indicates a monotropic phase observable on cooling only

Microphotographs of some characteristic textures of the SmC* phase obtained on cooling on non-homogenously aligned planar samples are presented in Figure 3. The texture of the SmC* phase with dechiralization lines corresponding to the helical pitch of about 1.7 μm is shown in Figure 3(a) for the compound **H 12/5** at 130°C. Peculiar is the texture of the partly unwound SmC* phase for the compound **H 12/8 at** 85°C in Figure 3(b). The width of the microphotographs for **H 12/5** and **H 12/8** is about 300 μm. The SmC* phase for **DM 7/10** at 44.0^{o}C is presented in Figure 3(c) (magnification = 80).
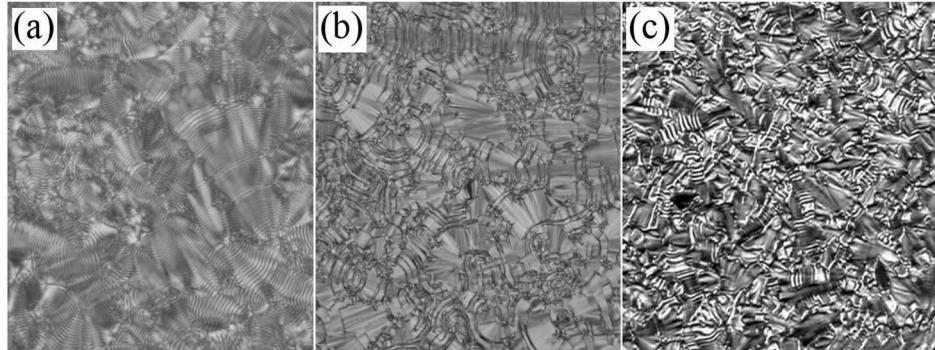
Figure 3. Microphotographs of SmC* textures for: (a) **H 12/5**, (b) **H 12/8** and (c) **DM 7/10**.

All investigated compounds possess fan-shaped textures exhibiting focal conic defects. The striations appear due to the periodical rotation of the director twist angle. Due to the optics, the separation of the stripes corresponds to the half-pitch of the smectic screw, instead of the full pitch (which is the actual periodicity of the structure) [18]. This texture is characteristic to the chiral smectic C* liquid crystal phase, and most commonly (but not exclusively) shows up after the transition from the SmA* phase exhibiting plain fan-shaped texture. In this striated fan-shaped texture the surface area is occupied by the polygonal base of a focal conic domain. However, formation of such domains, although it reduces the surface energy, is also accompanied by an increase of the "bulk" energy due to the director distortions. The energy balance dictates that the focal conic domains have to be larger than some critical size in order to become stable. Depending on the arrangement of focal conic domains, there will be an area where smectic layers are perpendicular to the bottom plate and tilted at the top plate (see Figure 4).
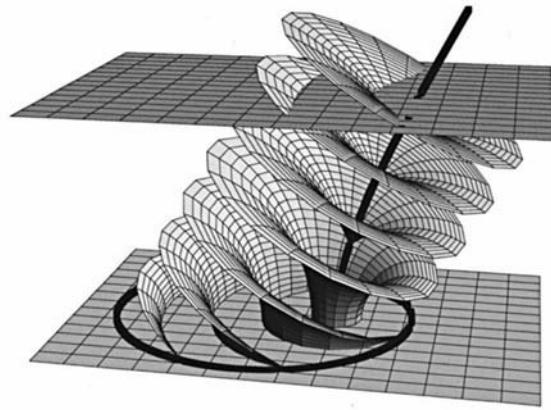

Figure 4. Schematic representation of a focal conic domain confined between two parallel plates.

X-ray diffraction studies have been carried out on all investigated compounds. Selected wide angle X-ray diffraction powder patterns, obtained on cooling from the isotropic phase, are shown in Figure 5.

The analysis of X-ray diagrams for the investigated compounds confirms that all substances of H- and QM-series exhibit a broad temperature range of the tilted ferroelectric smectic SmC* phase. The presence of a reflection peak at small angles indicates the layer structure of layer thickness d; the diffuse outer scattering corresponds to the average intermolecular distance D between the long axes of the neighbouring parallel molecules.

Some phases exhibit a relatively strong second order reflection peak and a weak third-order reflection peak, thus indicating a more ordered arrangement of the molecules. For **H 12/8** in the SmB* phase, the sharp first-order reflection peak is detected at $2\theta = 2.4^o$, a relatively strong second- and third-order reflection peaks appear at $2\theta = 3.9^o$ and $2\theta = 5.7^o$ respectively. In addition, the appearance of a strong reflection at the wide angle is an important indication for the existence of a positional order of the molecules within the smectic layers.
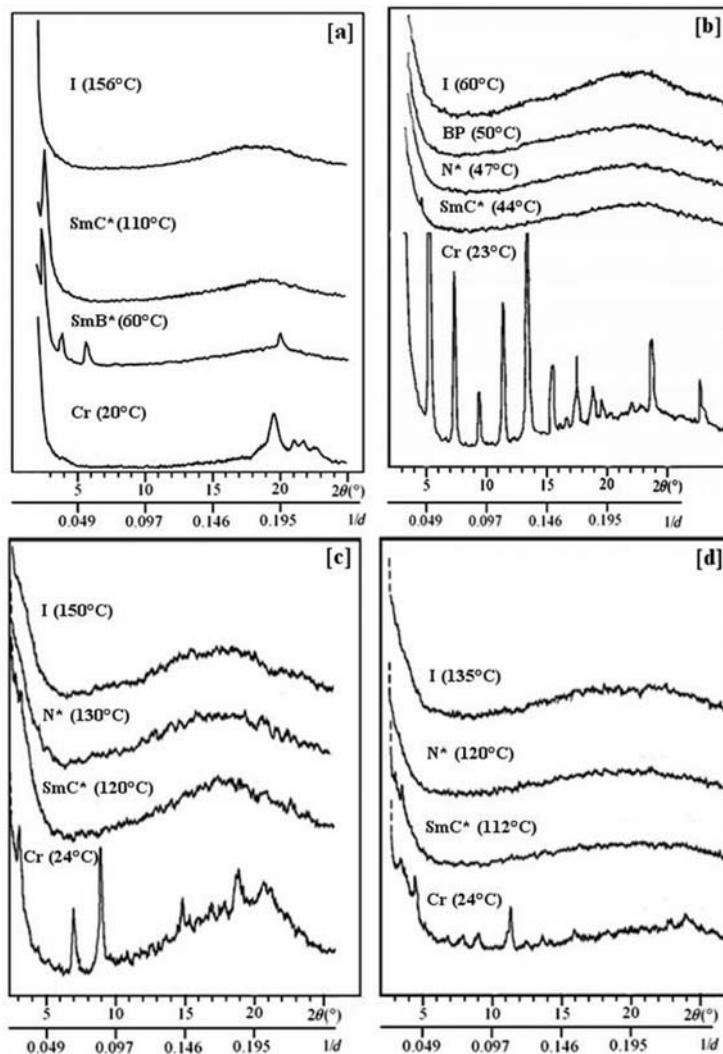

Figure 5. X-ray diffraction profiles for (a) **H 12/8**, (b) **DM 7/10**, (c) **QM 10/10**, (d) **QM 12/9**.

For **H 12/8**, the peak at $2\theta = 20^o$ (see Figure 5a) corresponds to the hexagonal packing

of the centres of mass of the molecules in the smectic layers, which is a characteristic feature of the SmB* phase. At the temperature of the SmC*→ SmB* phase transition, the change from tilted to orthogonal phase is the reason for the increase in the layer spacing (See Table 3).

Table 3. Molecular parameters of some compounds for all the studied phases at the indicated temperature $T(^oC)$; angles corresponding to the reflection peaks $2\theta(^o)$; effective layer thickness $d(\text{Å})$ (error of measurements δd was about ± 0.5 Å); average repeat distance $D(\text{Å})$ (error of measurements δD was about ± 0.02 Å); intermolecular distance $b(\text{Å})$.

Compound	Phase	$T(^oC)$	$2\theta(^o)$	$d(\text{Å})$	$D(\text{Å})$	$b(\text{Å})$
H 12/8	Iso	156.0	18.0	-	5.726	-
	SmC*	110.0	2.5	41.06	-	-
			19.0	-	5.427	-
	SmB*	60.0	2.4	42.77	-	-
			3.9	26.32	-	-
			5.7	18.02	-	-
			20.0	-	5.158	5.956
DM 10/12	Iso	60.0	21.1	-	4.888	-
	SmC*	52.0	4.4	23.1	-	-
			5.3	19.4	-	-

The centres of the wide diffuse outer scattering consistently shift toward higher angles with temperature decrease, thus indicating an increase in the packing density (a decrease of the average lateral intermolecular distance between the long axis of the neighbouring molecules) for the isotropic, chiral nematic and ferroelectric SmC* phases for all studied compounds.

At a low temperature, for the orthogonal hexatic SmB* phase of H-series, the average intermolecular distance between the long axes of neighbouring parallel molecules has been calculated as $b = 2D/3^{1/2}$ [18-22].

While decreasing the temperature, the position of the small angle reflection is somewhat shifted to higher angles, indicating a decrease in layer spacing of the SmC* phase for all studied compounds.

The MOPAC/AM1 model was used to calculate the length of the H 12/8 molecule in the energy-optimized conformation [16]. Taking into account the most extended conformer, the length of the molecules L is found to be about 42 Å for the **H 12/8** compound. The calculated molecular length agrees very well with the values of the layer spacing. The molecule is 1 Å longer than the determined layer thickness, thus indicating tilting of the molecules to create smectic layers of the chiral smectic C phase.

The total length of the **DM 10/12** molecule was calculated by the semi-empirical CAChe/MOPAC/PM5 method (Figure 6) [17]. This approximation gave 45 Å in length of the all trans conformations. This value interpreted together with the layer spacing of 23 Å shows evidently an intercalated structure appearing in its chiral smectic phase. Intercalation is the preferable mode of packing, because the two lateral methyl groups forbid stacking of rigid inner cores of molecules of the DM-series. The same method of

intercalated packing is not encountered in the H- and QM-series, which by reason of their narrower rigid cores, are allowed to pack in a dense fashion.
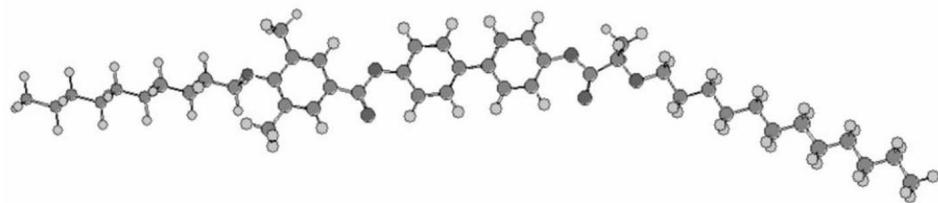

Figure 6. Optimized structure of **DM 10/12**.

4. Conclusion

The mesomorphic and structural properties of the homologue series of ferroelectrics liquid crystals with one chiral centre, the 2-alkoxypropionate chiral group, have been studied. A broad temperature range of the ferroelectric SmC* phase has been detected for all investigated substances of the H- and QM-series.

With the decrease of temperature, the tilt of the molecules with respect to the layer normal increases, thus causing the decrease in the layer thickness of the SmC* phase for all studied compounds (see [15-17] for more details).

Lateral substitution by two methyl groups discourages close packing in the DM-series with respect to the H- and QM-series, promoting intercalation instead, which subsequently disrupts the stability of the ferroelectric SmC* phase, resulting in a decrease of its phase transition temperatures and simultaneous decrease of its temperature range.

Due to a broad range and high thermal stability of the ferroelectric phase in the QM and H series, compounds studied in this work can potentially be used as chiral dopants in the multicomponent mixtures for photonic applications.

Acknowledgments

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